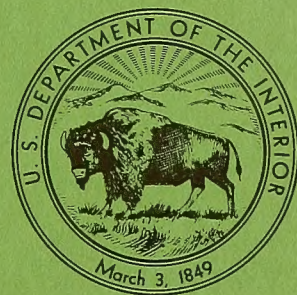


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Properties of Seawater and its Concentrates and Related Solutions at Temperatures up to 400° F.

United States Department of the Interior



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Properties of Seawater and its Concentrates and Related Solutions at Temperatures up to 400° F.

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for Office of Saline Water, J. W. O'Meara, Acting Director;
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OSW Grant No. 14-30-2525

MBL/WHOI



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United States Department of the Interior • Rogers C. B. Morton, Secretary
James R. Smith, Assistant Secretary for Water and Power Resources

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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

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NOMENCLATURE

A_H	Debye-Hückel constant for enthalpy
A_j	Debye-Hückel constant for heat capacity
B, B', B''	Constant
C''	Constant
C_P	Heat capacity of solution at constant pressure, cal/gm°C
$\overline{C_{P_S}^{\circ}}$	Partial heat capacity of salts at infinite dilution cal/gm-salts-°C
$C_{P_W}^*$	Heat capacity of pure water, cal/gm-water-°C
C_S	Heat capacity of saturated solution, cal/gm°C
$f(C)$	Weighting function in equation (4)
H	Enthalpy of solution, cal.
I	Ionic strength = $(\sum m_i z_i^2)/2$
K	Heat capacity of calorimeter, cal/°C
$\overline{L_S}$	Partial enthalpy of salts in solution, cal/gm-salt
$\overline{L_W}$	Partial enthalpy of water in solution, cal/gm-water
M_i	Molecular weight of ion i
M_S	Molecular weight of solvent
m_i	Molality of ion i, gm-mol/1000 gm-solvent
m_+	Molality of positive ion
m_-	Molality of negative ion
$P(C)$	Any concentration dependent property in eqn (4)
r	Resistance, absolute ohms

R	Universal gas constant; ratio of conductivity
R_t	Conductivity ratio at $t^\circ\text{C}$, as defined on p
$(\text{RH})^t$	Relative enthalpy at $t^\circ\text{C}$, cal/gm
S	Salinity, Weight percent
S°/oo	Salinity, Gm/kg solution
T	Temperature, $^\circ\text{K}$
t	Temperature, $^\circ\text{C}$; time, sec.
t_o	Hypothetical firing time, min.
$\bar{V}_S$	Partial molal volume
x	Mass fraction of salts in solution = $.01 \times S\%$
Z_i	Charge on ion i
$\sigma(I^{1/2})$	$= \frac{3}{I^{3/2}} \left(1 + I^{1/2} - \frac{1}{1 + I^{1/2}} - 2 \ln(1 + I^{1/2}) \right)$
ϕC_{p_S}	Apparent heat capacity of salts, cal/gm-salt $^\circ\text{C}$
ϕL_S	Apparent enthalpy of salts in solution, cal/gm salt
π	Osmotic pressure of solution
ϕ	Osmotic coefficient

Summary

Heat capacity measurements are reported for NaCl, KCl, MgSO₄, Na₂SO₄ and MgCl₂ solutions. Heats of mixing for sea salt solutions are reported for 73°C. These values are reasonably consistent with enthalpy values previously published (1).

A limited number of experimental boiling point elevations of sea salt solutions between 80 and 120°C are reported. These are thought to be accurate to $\pm 0.001^\circ\text{C}$.

Kinematic viscosity values for sea salt solutions to 11% salinity between 0 and 150°C are reported. The values should be accurate to ± 0.002 centistokes.

HEAT CAPACITY

The basic theory and equipment details have been published previously (1) (2). An external view of the gold-plated beryllium-copper alloy bomb, which contains the sample under investigation, is shown in Figure 1. The apparent dullness in the lower portion of the bomb is due to specular reflection of the paper on which it is setting. Figure 2, a photograph of the interior gold plate, shows rather severe etching. In spite of this, the results appear to be reasonable and no failure of the bomb proper has taken place in over four years of intermittent use.

The heater, which has failed once and has been replaced, is shown in Figure 3. It consists of 360 cm of Nichrome V wire with a resistance of about 110 ohms housed in an Inconel-W tube but electrically insulated from it by magnesium oxide insulation. The entire heater is wound helically on a gold-plated copper frame. The solution is stirred by a slave magnet housed in a monel can shown in the center of Figure 3. The master magnet is driven at 300 rpm.

Figure 4 is a photograph of the constant temperature oven which contains the bomb. The auxiliary equipment consisting of a mechanical and diffusion pump is shown in the foreground. Vacuum is measured by two thermocouple gauges connected to a Hughes TGC/100 indicator and a cold cathode discharge gauge connected to a Hughes PGC-200 indicator.

A view of the potentiometers and recording system with several typical recordings is shown in Figure 5.

The platinum resistance thermometer was built by Leeds and Northrup by placing a standard resistance element into a customized gold-plated copper tube. A scale drawing of the latter is shown in Figure 6. As shown, the top part of the tubing is made of beryllium copper. Two thermometers have been used in the reported data. These were calibrated by the National Bureau of Standards. The first thermometer, (which eventually broke down) which was used in the study of NaCl, had a resistance in absolute ohms given by

$$r = 25.4995 (1 + 0.0039855313T - 0.5856 \times 10^{-6}t^2) \quad (1)$$

Here, t is given in degrees Centigrade and, between 0°C and 200°C , the precision is guaranteed to be 1 part in 5000.



Figure 1

BOMB CALORIMETER USED FOR HEAT CAPACITY MEASUREMENTS



Figure 2

BOMB CALORIMETER INTERIOR



Figure 3
BOMB CALORIMETER HEATER

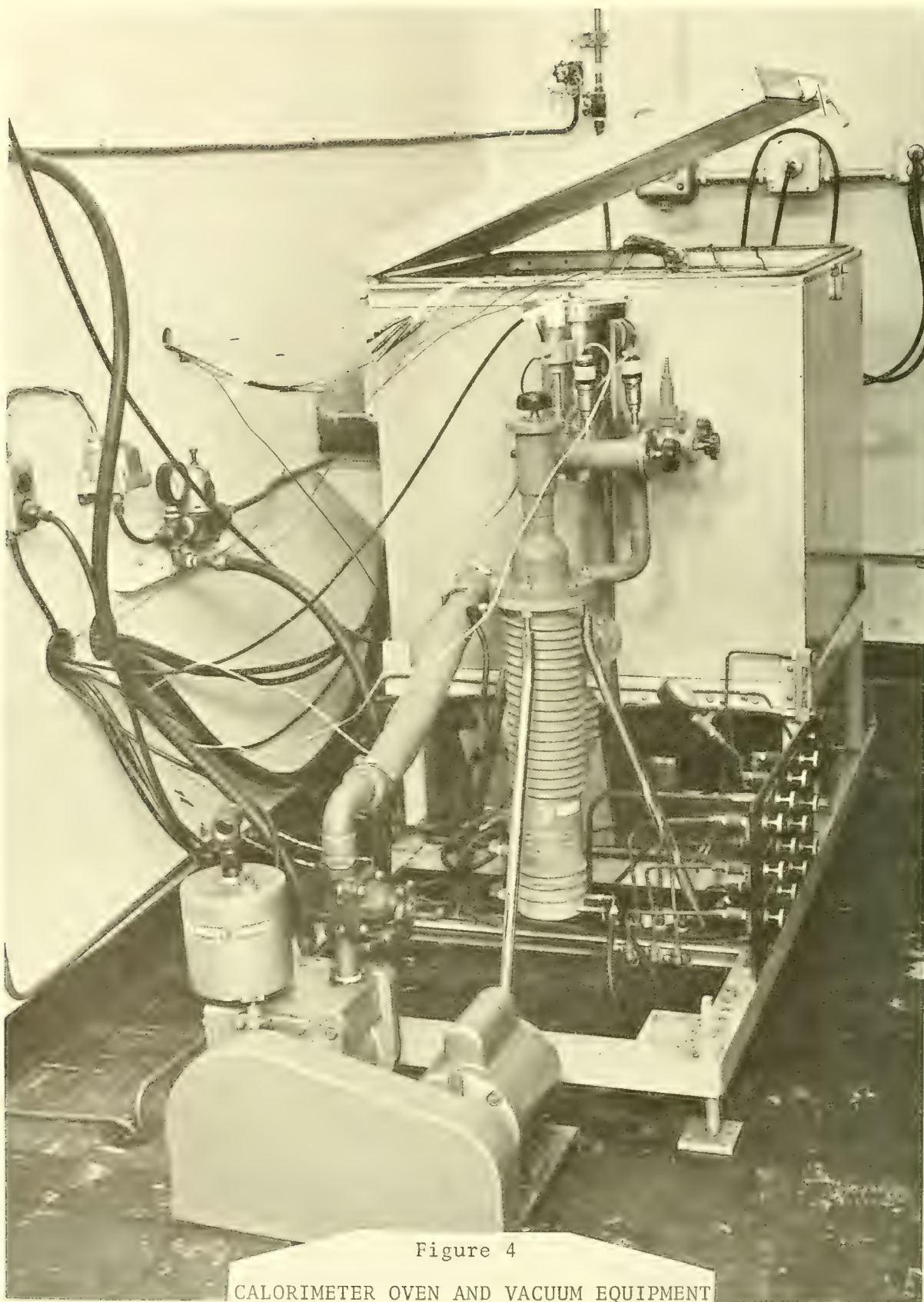


Figure 4

CALORIMETER OVEN AND VACUUM EQUIPMENT

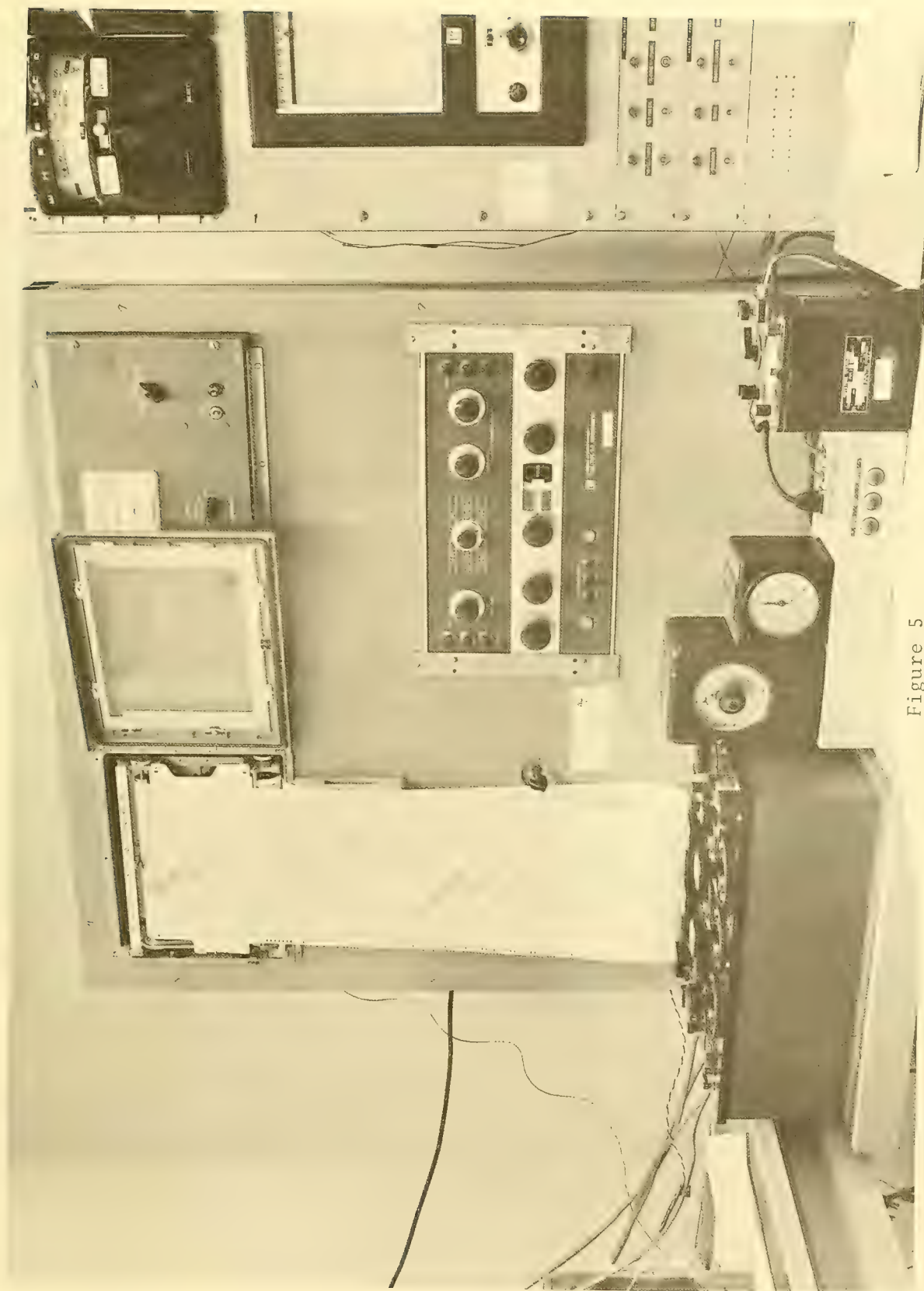


Figure 5

POTENTIOMETER AND RECORDING SYSTEM FOR THE HEAT CAPACITY CALORIMETER

The second thermometer, which was calibrated in July, 1970, has a resistance given by

$$r = 25.5390 (1 + 0.003982850T - 0.5730 \times 10^{-6}t^2) \quad (2)$$

The latter has been used in the study of all salt solutions except those of NaCl and KCl. The thermometer has four leads directly connected to a Mueller bridge which, for resistance changes less than one ohm, have an accuracy of 0.00001 ohm. All resistances are measured in accordance with calibration procedures of the National Bureau of Standards and recorded by a Leeds and Northrup Speedomax W recorder. The bridge is maintained at 34.8°C by a constant temperature control unit. At full sensitivity, it is possible to read the scale of the null detector to 0.0002°C.

Experimental Procedure

Calibration runs: Based on the heat capacity data for pure water by Osborne et al. (3) the heat capacity of the bomb calorimeter is determined.

The bomb calorimeter is first filled with an accurately-weighed quantity of distilled water. Then, starting from 80°C and with a progressive interval of 20°C, heat capacities are measured to 200°C. Depending on the reproducibility of the data, sets of runs are repeated from four to six times. A least squares smooth straight line is fitted through the data which is finally used in the computations of the heat capacities of any of the salt solutions under study.

Along with the calorimeter heat capacity, another item of information obtained during calibration is the hypothetical firing time. This is necessary in heat capacity measurements because there is heat transfer during the heat-input period and the input time is far from instantaneous. The usual procedure for determining the hypothetical firing time is extrapolating both the heating and the cooling curves to a certain time, t_0 , at which time the areas 1 and 2 in Figure 7 are equal.

Typical calibration results are presented in Table 1 for both the heat capacity of the calorimeter and the hypothetical firing time. Here K equals heat capacity of the calorimeter and t_0 is in minutes.

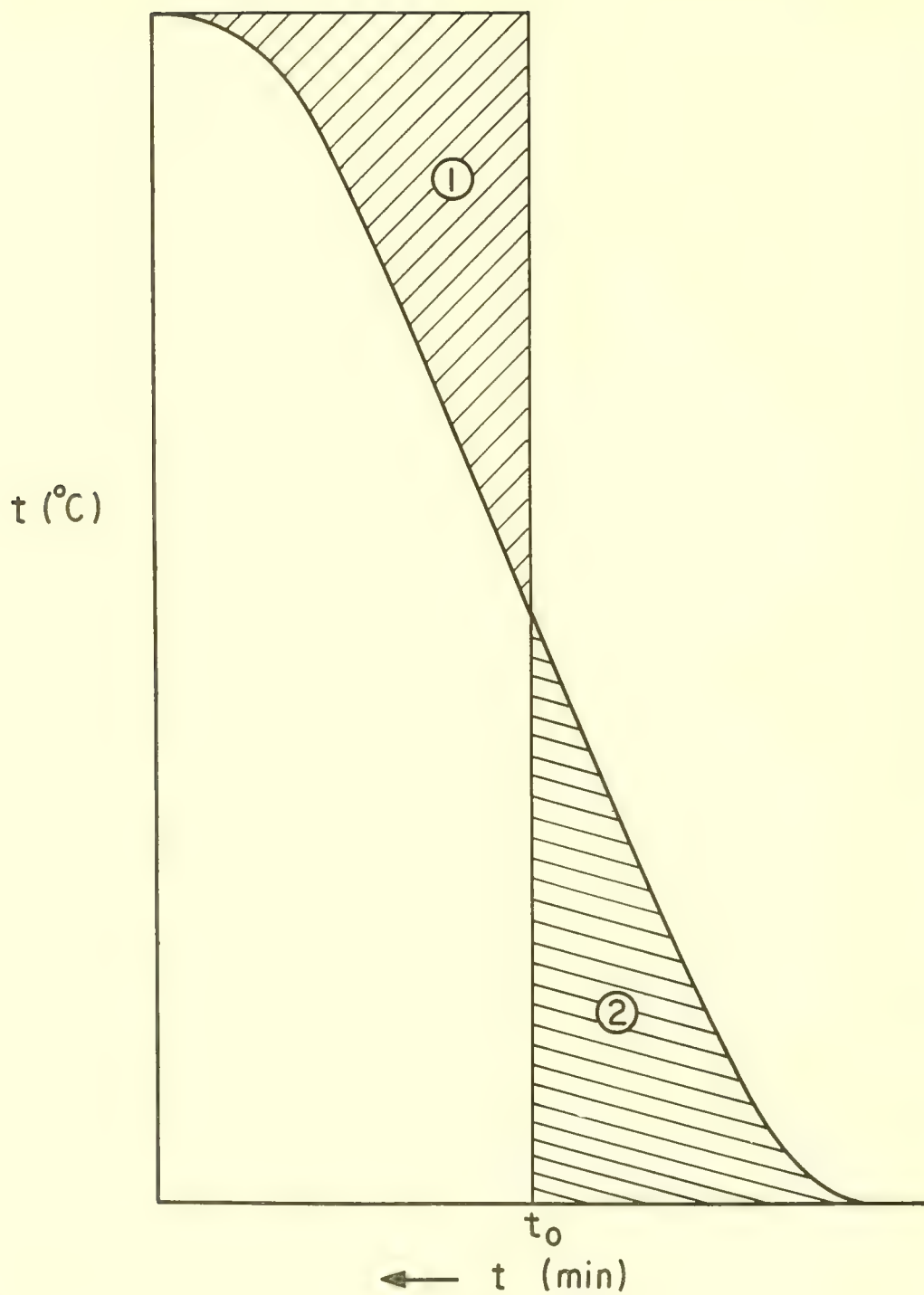


Figure 7
HYPOTHETICAL FIRING TIME

Table 1

Calibration Results for Heat Capacity and
Hypothetical Firing Time of
Bomb Calorimeter

	Temperature (°C)						
	<u>80</u>	<u>100</u>	<u>120</u>	<u>140</u>	<u>160</u>	<u>180</u>	<u>200</u>
K _{smooth}	286.1	288.7	291.3	293.9	296.5	299.1	301.7
t _o	1.22	1.24	1.25	1.27	1.25	1.22	1.20

Once the calibration results are ready, then runs on the desired salts continue. As mentioned earlier, all data measured are at saturation conditions, namely heat capacity at saturation (C_S). The C_S values are converted to C_P (heat capacity at constant pressure) by the use of Equation 3 and the steam tables.

$$C_P - C_S = T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_S \quad (3)$$

Results: To date, work on four electrolyte salts have been completed. These are NaCl, KCl, MgSO₄ and Na₂SO₄. Some data on MgCl₂ is also included. Tables 2-6 give the results obtained. In the tables, at each concentration (salinity) and each temperature, the first row gives values of saturation heat capacities, while the second row gives constant pressure heat capacities. In addition, along with each table some polynomial equations obtained from the curve fitting are given for both sets of values. The concentration, S ‰ (salinity) is defined as grams of solute (salts) per kilogram of solution (salts plus water). Values will, however, be expressed in percent, S%, (grams/100 grams solution). Lastly, included also are four sets of C_S vs. T graphs corresponding to the four salts, Figures 8-11.

HEATS OF MIXING OF SEA SALT SOLUTIONS

The purpose of this study was to report data on the heats of mixing and relative enthalpies of sea water solutions for a wide range of concentrations and

Table 2a

Heat Capacities for NaCl Solutions, Experimental

Temperatures (°C)											
S%	80	100	120	140	160	180	200				
	C _S C _P	C _S C _P	C _S C _P	C _S C _P	C _S C _P	C _S C _P	C _S C _P				
1.986	0.9792	0.9836	0.9893	0.9959	1.0063	1.0188	1.0330				
	0.9793	0.9838	0.9898	0.9969	1.0081	1.0220	1.0384				
3.32	0.9646	0.9686	0.9728	0.9795	0.9886	0.9997	1.0147				
	0.9647	0.9688	0.9733	0.9804	0.9903	1.0028	1.0199				
4.98	0.9478	0.9504	0.9538	0.9599	0.9681	0.9783	0.9908				
	0.9479	0.9506	0.9543	0.9608	0.9698	0.9812	0.9956				
8.41	0.9108	0.9142	0.9161	0.9206	0.9270	0.9350	0.9451				
	0.9109	0.9144	0.9165	0.9214	0.9284	0.9375	0.9492				
11.09	0.8879	0.8890	0.8913	0.8948	0.8997	0.9053	0.9141				
	0.8880	0.8892	0.8917	0.8955	0.9010	0.9075	0.9179				

Table 2b

Heat Capacities (Power Series Fit) for NaCl Solutions, Smoothed

S%	Temperatures (°C)								Standard Deviation						
	80		100		120		140			160		180		200	
	C _S	C _P	C _S	C _P	C _S	C _P	C _S	C _P		C _S	C _P	C _S	C _P	C _S	C _P
1.986	0.9793	0.9834	0.9890	0.9966	1.0063	1.0184	1.0332	3.66 x 10 ⁻⁴							
	0.9794	0.9836	0.9895	0.9975	1.0081	1.0216	1.0386	3.39 x 10 ⁻⁴							
3.32	0.9647	0.9683	0.9731	0.9796	0.9883	0.9998	1.0147	2.18 x 10 ⁻⁴							
	0.9648	0.9685	0.9735	0.9805	0.9900	1.0029	1.0199	1.93 x 10 ⁻⁴							
4.98	0.9479	0.9501	0.9540	0.9600	0.9680	0.9782	0.9908	1.85 x 10 ⁻⁴							
	0.9480	0.9503	0.9545	0.9609	0.9697	0.9812	0.9956	1.65 x 10 ⁻⁴							
8.41	0.9111	0.9134	0.9166	0.9209	0.9268	0.9348	0.9452	4.18 x 10 ⁻⁴							
	0.9112	0.9137	0.9170	0.9217	0.9282	0.9373	0.9493	4.07 x 10 ⁻⁴							
11.09	0.8878	0.8892	0.8914	0.8947	0.8994	0.9057	0.9139	2.41 x 10 ⁻⁴							
	0.8879	0.8894	0.8917	0.8954	0.9007	0.9080	0.9177	2.70 x 10 ⁻⁴							

$$S = 3.32\%: C_S = 0.9514 + 0.2441 \times 10^{-3}t - 0.1860 \times 10^{-5}t^2 + 0.1111 \times 10^{-7}t^3$$

$$C_P = 0.9480 + 0.3425 \times 10^{-3}t - 0.2833 \times 10^{-5}t^2 + 0.1458 \times 10^{-7}t^3$$

Table 3a

Heat Capacities for KCl Solutions, Experimental

S%	Temperatures (°C)							
	80	100	120	140	160	180	200	
	C _S C _P	C _S C _P	C _S C _P	C _S C _P	C _S C _P	C _S C _P	C _S C _P	
2.054	0.9776 0.9777	0.9813 0.9815	0.9865 0.9870	0.9946 0.9956	1.0049 1.0067	1.0187 1.0219	1.0362 1.0416	
4.098	0.9539 0.9540	0.9584 0.9586	0.9624 0.9629	0.9698 0.9707	0.9787 0.9804	0.9906 0.9936	1.0051 1.0101	
6.072	0.9307 0.9308	0.9343 0.9345	0.9394 0.9398	0.9459 0.9467	0.9543 0.9559	0.9654 0.9682	0.9767 0.9813	
8.148	0.9088 0.9089	0.9130 0.9132	0.9182 0.9186	0.9233 0.9241	0.9314 0.9328	0.9403 0.9428	0.9527 0.9569	
10.111	0.8847 0.8848	0.8890 0.8892	0.8935 0.8939	0.8986 0.8993	0.9055 0.9068	0.9135 0.9158	0.9243 0.9282	

Table 3b

Heat Capacities (Power Series) for KCl Solutions, Smoothed

S%	Temperatures (°C)										Standard Deviation				
	80		100		120		140		160			180		200	
	C _S	C _P	C _S	C _P	C _S	C _P	C _S	C _P	C _S	C _P		C _S	C _P	C _S	C _P
2.054	0.9776	0.9812	0.9867	0.9944	1.0050	1.0187	1.0362	1.07 x 10 ⁻⁴							
	0.9777	0.9815	0.9872	0.9954	1.0068	1.0220	1.0416	1.18 x 10 ⁻⁴							
4.098	0.9541	0.9578	0.9629	0.9697	0.9787	0.9904	1.0052	3.29 x 10 ⁻⁴							
	0.9542	0.9581	0.9634	0.9706	0.9804	0.9934	1.0102	3.05 x 10 ⁻⁴							
6.072	0.9308	0.9342	0.9393	0.9461	0.9546	0.9649	0.9769	2.82 x 10 ⁻⁴							
	0.9309	0.9344	0.9397	0.9469	0.9562	0.9677	0.9815	2.80 x 10 ⁻⁴							
8.148	0.9088	0.9131	0.9179	0.9237	0.9310	0.9405	0.9527	2.68 x 10 ⁻⁴							
	0.9089	0.9134	0.9183	0.9245	0.9325	0.9430	0.9568	2.58 x 10 ⁻⁴							
10.111	0.8847	0.8890	0.8935	0.8987	0.9053	0.9136	0.9243	1.18 x 10 ⁻⁴							
	0.8848	0.8892	0.8939	0.8994	0.9066	0.9159	0.9282	1.22 x 10 ⁻⁴							

$$S = 4.098\%: C_S = 0.9431 + 0.1726 \times 10^{-3}t - 0.1185 \times 10^{-5}t^2 + 0.9375 \times 10^{-8}t^3$$

$$C_P = 0.9402 + 0.2585 \times 10^{-3}t - 0.2042 \times 10^{-5}t^2 + 0.1250 \times 10^{-7}t^3$$

Table 4a

Heat Capacities for MgSO_4 Solutions, Experimental

		Temperatures ($^{\circ}\text{C}$)					
$S\%$		80	100	120	140	160	180
		C_S C_P	C_S C_P	C_S C_P	C_S C_P	C_S C_P	C_S C_P
3.989%		0.9609 0.9610	0.9675 0.9677	0.9756 0.9761	0.9859 0.9868	0.9988 1.0005	1.0147 1.0177
6.029%		0.9409	0.9482	0.9571	0.9675	0.9816	0.9982
		0.9410	0.9484	0.9575	0.9683	0.9832	1.0010
8.001%		0.9223	0.9307	0.9401	0.9517	0.9654	0.9824
		0.9224	0.9309	0.9405	0.9525	0.9668	0.9849
9.994%		0.9050	0.9135	0.9236	0.9348	0.9497	0.9676
		0.9051	0.9137	0.9240	0.9355	0.9510	0.9699
		90°	100°	130°	140°	160°	180°
2.101%		0.9835	0.9864	0.9979	1.0037	1.0154	1.0309
		0.9836	0.9866	0.9986	1.0047	1.0172	1.0341
							200°
							1.0502
							1.0556

Table 4b

Heat Capacities (Power Series) for MgSO_4 Solutions, SmoothedTemperatures ($^{\circ}\text{C}$)

S%	80		100		120		140		160		180		Standard Deviation	
	C _S	C _P	C _S	C _P	C _S	C _P	C _S	C _P	C _S	C _P	C _S	C _P		
3.989%	0.9616	0.9616	0.9665	0.9665	0.9754	0.9754	0.9867	0.9867	0.9985	0.9985	1.0147	1.0147	6.71 x 10 ⁻⁴	
	0.9617	0.9617	0.9667	0.9667	0.9759	0.9759	0.9877	0.9877	1.0001	1.0001	1.0177	1.0177	7.08 x 10 ⁻⁴	
6.029%	0.9417	0.9417	0.9471	0.9471	0.9567	0.9567	0.9687	0.9687	0.9811	0.9811	0.9982	0.9982	8.66 x 10 ⁻⁴	
	0.9418	0.9418	0.9472	0.9472	0.9571	0.9571	0.9696	0.9696	0.9827	0.9827	1.0010	1.0010	9.13 x 10 ⁻⁴	
8.001%	0.9231	0.9231	0.9294	0.9294	0.9400	0.9400	0.9527	0.9527	0.9650	0.9650	0.9824	0.9824	8.15 x 10 ⁻⁴	
	0.9232	0.9232	0.9296	0.9296	0.9405	0.9405	0.9535	0.9535	0.9664	0.9664	0.9849	0.9849	8.38 x 10 ⁻⁴	
9.994%	0.9059	0.9059	0.9123	0.9123	0.9231	0.9231	0.9362	0.9362	0.9491	0.9491	0.9676	0.9676	9.78 x 10 ⁻⁴	
	0.9050	0.9050	0.9124	0.9124	0.9235	0.9235	0.9370	0.9370	0.9504	0.9504	0.9699	0.9699	1.02 x 10 ⁻³	
	90		100		130		140		160		180		200	standard Deviation
2.101%	0.9835	0.9835	0.9864	0.9864	0.9982	0.9982	1.0033	1.0033	1.0155	1.0155	1.0310	1.0310	1.0502	2.23 x 10 ⁻⁴
	0.9835	0.9835	0.9867	0.9867	0.9989	0.9989	1.0042	1.0042	1.0173	1.0173	1.0342	1.0342	1.0556	2.36 x 10 ⁻⁴
3.989%:	C _S = 1.0178 - 0.1760 x 10 ⁻² t + 0.1619 x 10 ⁻⁴ t ² - 0.3713 x 10 ⁻⁷ t ³													
	C _P = 1.0209 - 0.1834 x 10 ⁻² t + 0.1679 x 10 ⁻⁴ t ² - 0.3778 x 10 ⁻⁷ t ³													

Table 5a

Heat Capacities for Na_2SO_4 Solutions, Experimental

S%	Temperatures ($^{\circ}\text{C}$)							
	80		100		120		140	
	C_S	C_P	C_S	C_P	C_S	C_P	C_S	C_P
1.997%	0.9822	0.9861	0.9918	0.9997	1.0101	1.0239	1.0101	1.0239
	0.9823	0.9863	0.9923	1.0007	1.0119	1.0271	1.0119	1.0271
3.954%	0.9624	0.9662	0.9721	0.9789	0.9884	1.0007	0.9884	1.0007
	0.9625	0.9664	0.9726	0.9798	0.9901	1.0037	0.9901	1.0037
5.957%	0.9442	0.9481	0.9526	0.9598	0.9678	0.9798	0.9678	0.9798
	0.9443	0.9483	0.9530	0.9606	0.9694	0.9826	0.9694	0.9826
7.952%	0.9271	0.9317	0.9355	0.9411	0.9492	0.9588	0.9492	0.9588
	0.9272	0.9319	0.9359	0.9419	0.9516	0.9613	0.9516	0.9613
9.882%	0.9114	0.9146	0.9182	0.9240	0.9312	0.9405	0.9312	0.9405
	0.9115	0.9148	0.9186	0.9247	0.9325	0.9428	0.9325	0.9428

Table 5b

Heat Capacities (Power Series) for Na₂SO₄ Solutions, Smoothed

Temperatures (°C)

S %	80		100		120		140		160		180		Standard Deviation
	C _S	C _P	C _S	C _P	C _S	C _P	C _S	C _P	C _S	C _P	C _S	C _P	
1.997%	0.9826	0.9855	0.9917	1.0002	1.0099	1.0239	1.0013	1.0117	1.0271	1.0407	1.0537	1.0677	4.13 x 10 ⁻⁴
3.954%	0.9827	0.9857	0.9922	1.0013	1.0117	1.0271	1.0326	1.0481	1.0636	1.0791	1.0946	1.1101	4.37 x 10 ⁻⁴
5.957%	0.9628	0.9658	0.9718	0.9796	0.9881	1.0007	0.9906	0.9998	1.0124	1.0250	1.0376	1.0502	4.40 x 10 ⁻⁴
7.952%	0.9629	0.9659	0.9722	0.9806	0.9898	1.0037	0.9600	0.9677	0.9798	0.9926	1.0054	1.0182	4.83 x 10 ⁻⁴
9.882%	0.9446	0.9474	0.9529	0.9600	0.9677	0.9798	0.9609	0.9693	0.9826	0.9958	1.0091	1.0224	3.99 x 10 ⁻⁴
	0.9447	0.9475	0.9533	0.9609	0.9693	0.9826	0.9419	0.9488	0.9588	0.9688	0.9788	0.9888	4.36 x 10 ⁻⁴
	0.9279	0.9305	0.9355	0.9419	0.9488	0.9588	0.9430	0.9511	0.9613	0.9713	0.9813	0.9913	7.60 x 10 ⁻⁴
	0.9281	0.9306	0.9358	0.9430	0.9511	0.9613	0.9243	0.9310	0.9405	0.9505	0.9605	0.9705	8.83 x 10 ⁻⁴
	0.9118	0.9139	0.9183	0.9243	0.9310	0.9405	0.9243	0.9310	0.9405	0.9505	0.9605	0.9705	3.94 x 10 ⁻⁴
	0.9119	0.9141	0.9187	0.9251	0.9323	0.9428	0.9251	0.9323	0.9428	0.9528	0.9628	0.9728	4.23 x 10 ⁻⁴

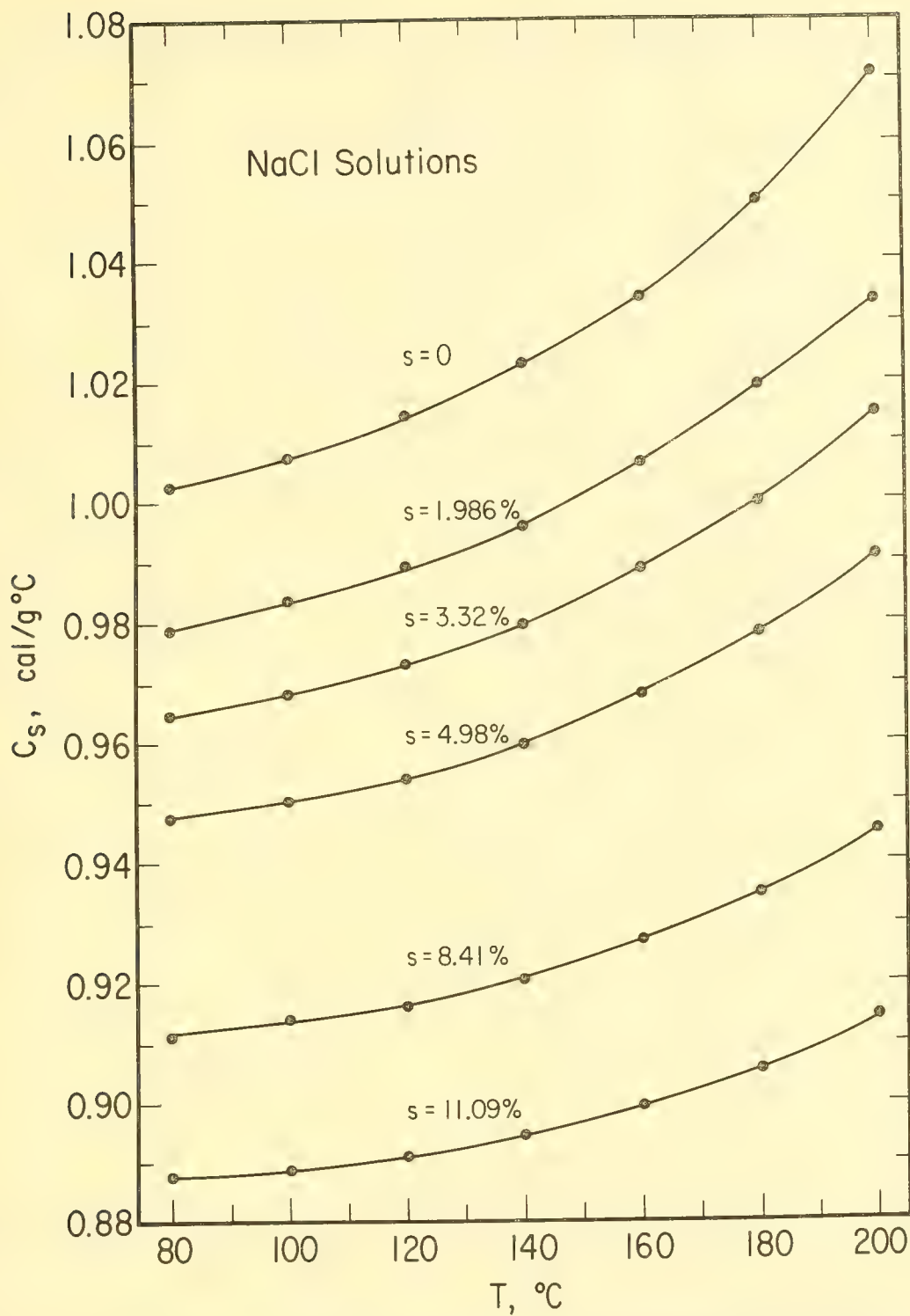
$$S = 3.954\%: C_S = 1.0028 - 0.1210 \times 10^{-2}t + 0.1073 \times 10^{-4}t^2 - 0.2341 \times 10^{-7}t^3$$

$$C_P = 1.0060 - 0.1284 \times 10^{-2}t + 0.1124 \times 10^{-4}t^2 - 0.2406 \times 10^{-7}t^3$$

Table 6

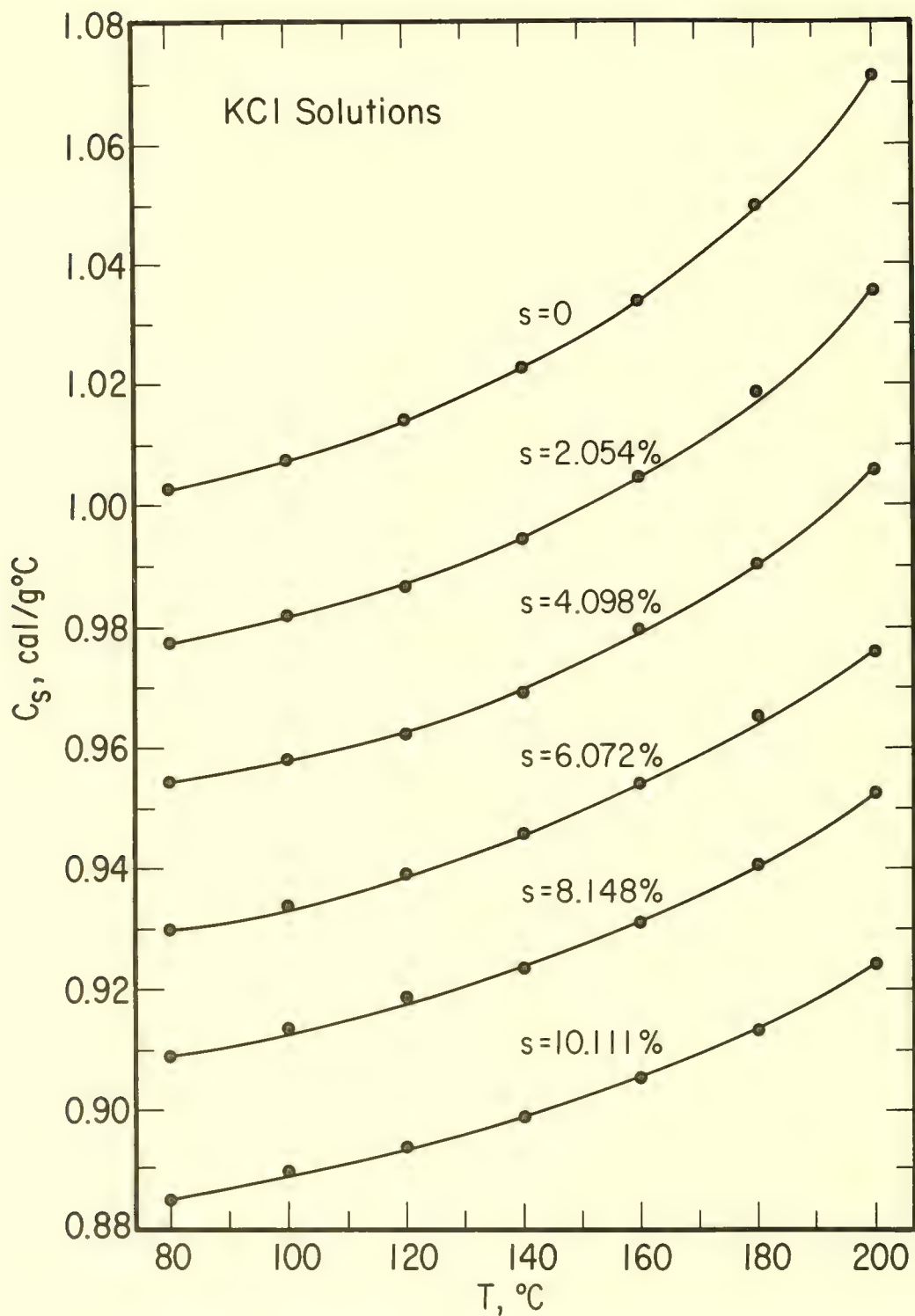
Heat Capacities at Thermal Saturation (C_S) for MgCl_2 Solutions,
Experimental

<u>S %</u>	<u>Temperatures ($^{\circ}\text{C}$)</u>				
	<u>80</u>	<u>100</u>	<u>120</u>	<u>140</u>	<u>180</u>
2.044%	0.9721	0.9791	0.9818	0.9890	1.0115
3.996%	0.9455	0.9495	0.9542	0.9609	0.9806



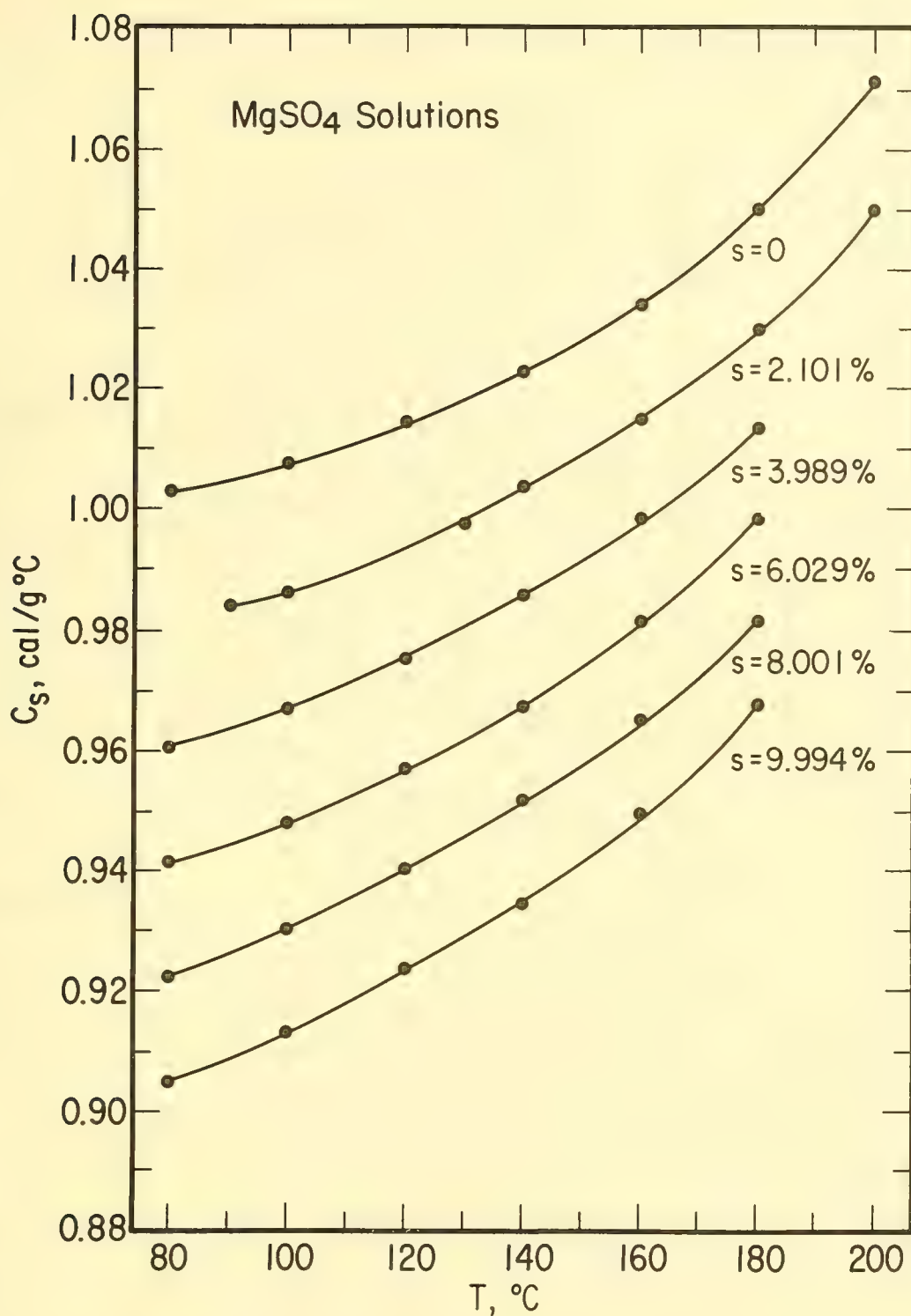
Experimental Values of Heat Capacity at Thermal Saturation

Figure 8



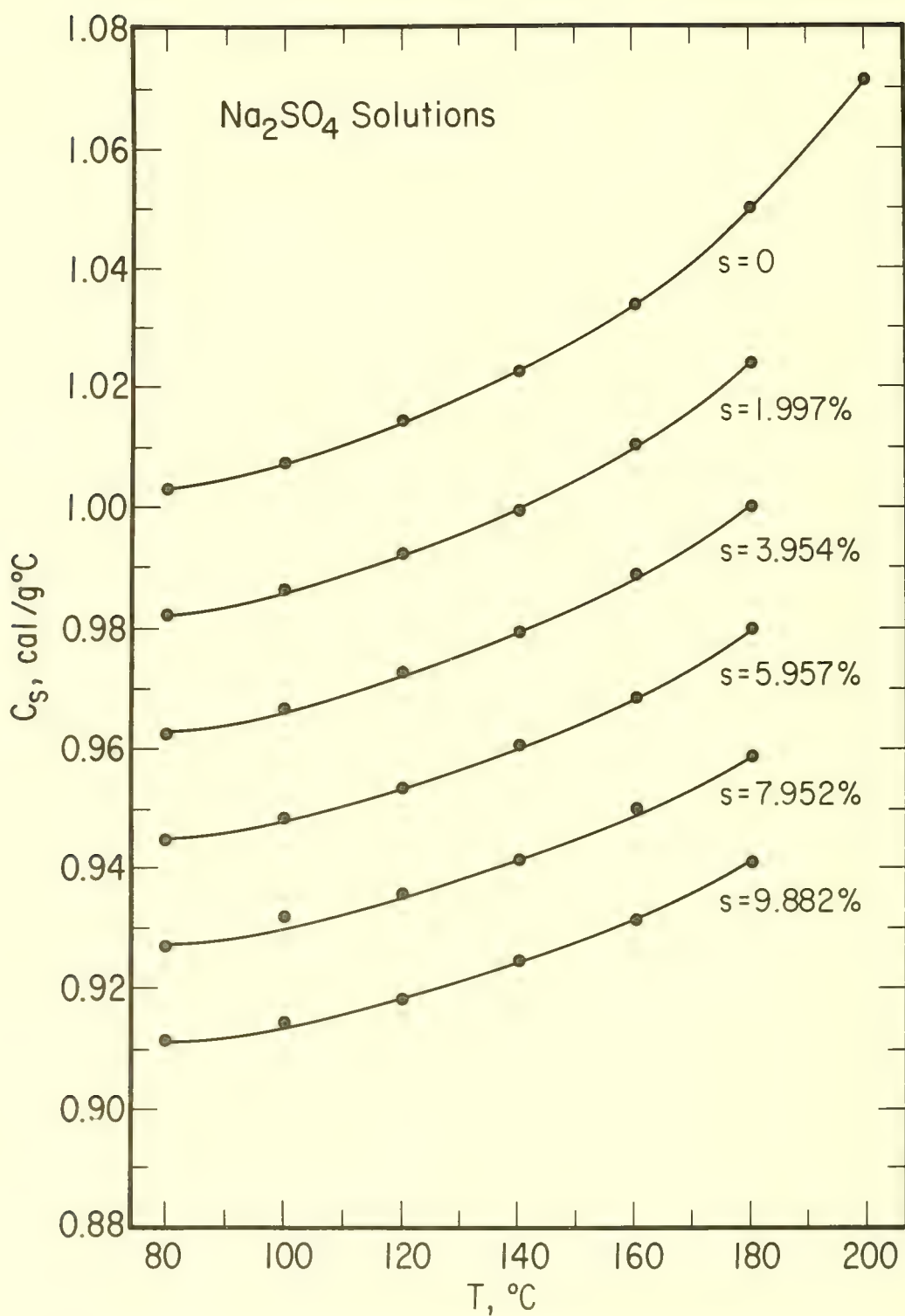
Experimental Values of Heat Capacity at Thermal Saturation

Figure 9



Experimental Values of Heat Capacity at Thermal Saturation

Figure 10



Experimental Values of Heat Capacity at Thermal Saturation

Figure 11

temperatures. Apart from its immediate importance in desalination related studies, the data are likely to be useful for the calculation of change of free energy of sea water with temperature and for variation of activity coefficients.

The relative enthalpies of sea salt solutions at 25°C (4) and at 50°C (2) have been reported in earlier publications. The results at 73°C are summarized in this report. Measurements at 3°C are in progress and will be presented in a subsequent publication.

Some effort has also been devoted to the development of a suitable mathematical expression for the relative enthalpies of sea salt solutions. The Debye-Hückel theory seems to be a reasonable starting base. Lange (5) has shown that the Debye-Hückel theory represents the heat of dilution data reasonably well for 1-1, 1-2, 2-1, 1-3, and 1-4 salts in the 0.001 molal to 0.01 molal range. To extend its validity to higher concentration ranges, many other approaches have been published which either had to do with the problem of finding a more exact expression for the coulombic interactions or which tried to include the other effects as well. These "extended" theories invariably introduced additional empirical parameters. In principle, similar results can be obtained mathematically by adding a power series to the expression derived from Debye-Hückel theory. Although a possible physical significance is lost, the experimental data can be correlated more easily. One such "extended model" has been developed and used in this work.

At still higher concentrations, even the "extended" theories fail to correlate the data satisfactorily. The Debye-Hückel theory considers only the long range interaction of ions. At higher concentrations, ion solvent interactions and short range interactions become far more significant, necessitating the development of an entirely different model, perhaps of a cell or lattice type structure, using the fused salt as the upper limit of concentration. Leitzke, Stoughton and Fouss (6) have suggested a weighted contribution of the two significant structures in the form:

$$P(C) = P(0)f(C) + P(\infty) [1 - f(C)] \quad (4)$$

where $P(C)$ is the value of a given property at concentration C , $P(0)$ is the Debye-Hückel description of that property and $P(\infty)$ represents the concentrated solution

value. The weighting function $f(C)$ has to satisfy the conditions $f(0) = 1$ and $f(\infty) = 0$ in order to ensure a smooth transition to the Debye-Hückel values at lower concentrations. The success of any such model hinges essentially on the right selection of the weighting function, $f(C)$. Attempts are being made to determine a suitable weighting function and to test the applicability of a similar model on sea salt solutions.

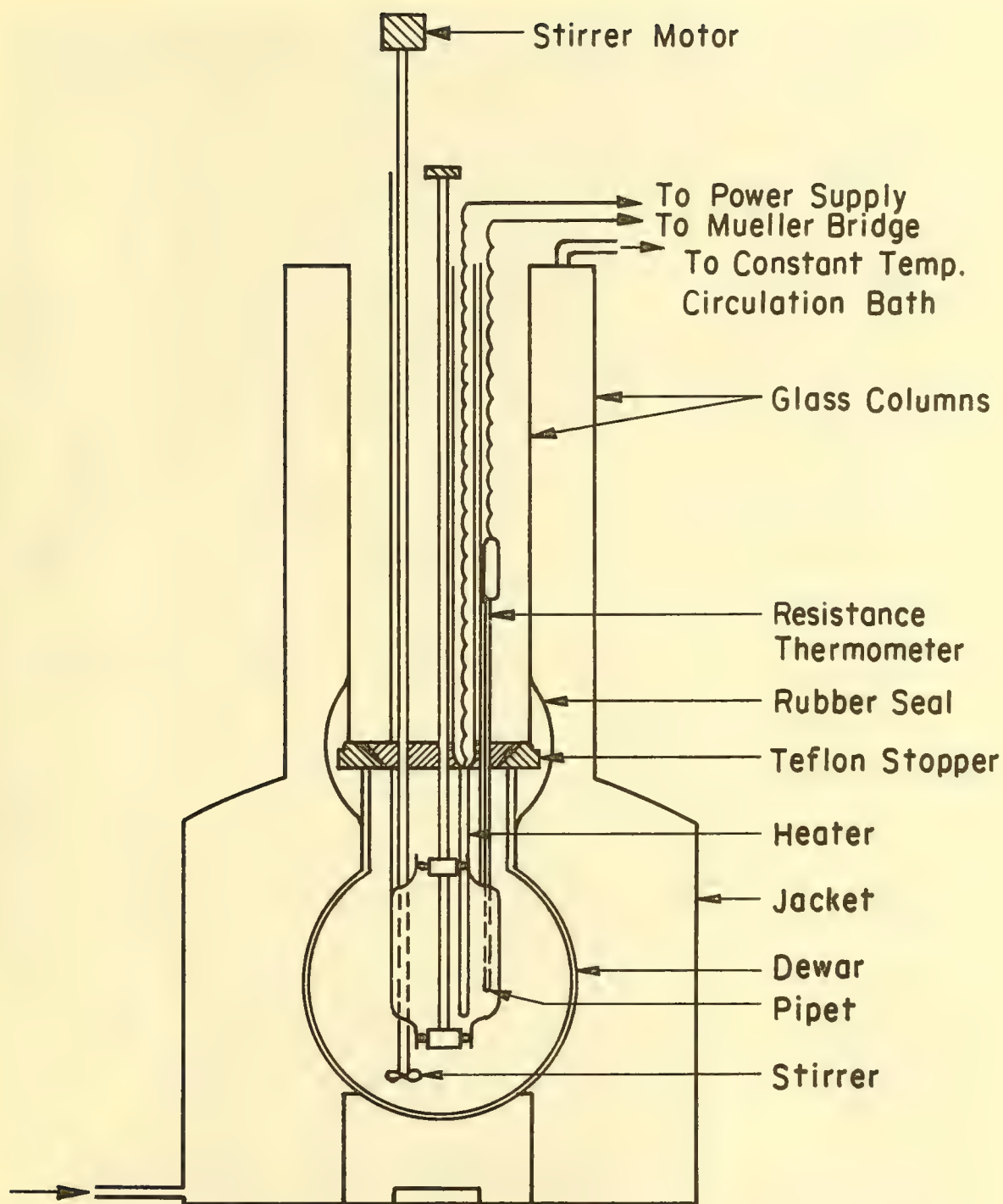
Experimental Procedure

Equipment: The primary element of the equipment is a well-stirred dewar of about four liters capacity which is filled with an accurately-weighed amount of one of the solutions to be mixed. The dewar is maintained at a fixed temperature by circulating constant temperature water around it. The temperature of circulating water is controlled by a Hallikainen thermotrol, aided by a Lauda constant temperature circulation bath. For low temperature measurements, the Lauda circulation bath was replaced by a K4R Lauda refrigeration bath. Glycerol-water-mixture was used as the circulation liquid.

The other solution to be mixed is contained in a stainless steel pipet (of about 170 cc capacity) immersed into the dewar vessel. The low pipet capacity ensures that the heat of mixing is not too large to upset the near isothermal operation. A Rosemount platinum resistance thermometer is immersed into the dewar for temperature measurements. The thermometer is connected to a magnetically shielded and thermally insulated Leeds and Northrup type G-2 Mueller bridge and a Keithley model 147 nanovolt detector, coupled to a Leeds and Northrup speedomax recorder.

A detailed description of the equipment is available in an earlier report (2). A sectional view of the calorimeter is reproduced in Figure 12. A photograph of the calorimeter and related equipment is shown in Figure 13 and a photograph of the stainless steel pipet and stirrer in Figure 14.

Salinity Determinations: The salinity of the sea salt solutions was measured by the conductometric method using a Bissett Berman model 6230 salinometer. The salinity, S°/oo is related to the conductivity by:



From Constant Temp.
Circulation Bath

Figure 12

SECTIONAL VIEW OF CALORIMETER FOR HEAT OF MIXING MEASUREMENTS

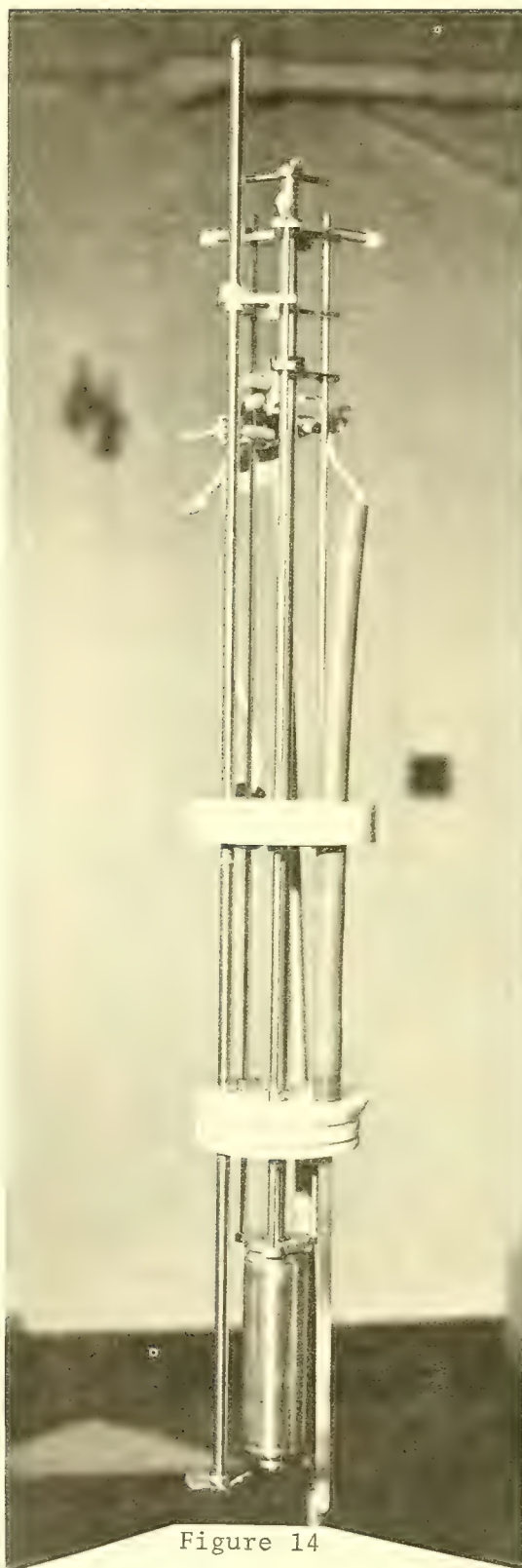


Figure 14

STAINLESS STEEL PIPET AND STIRRER

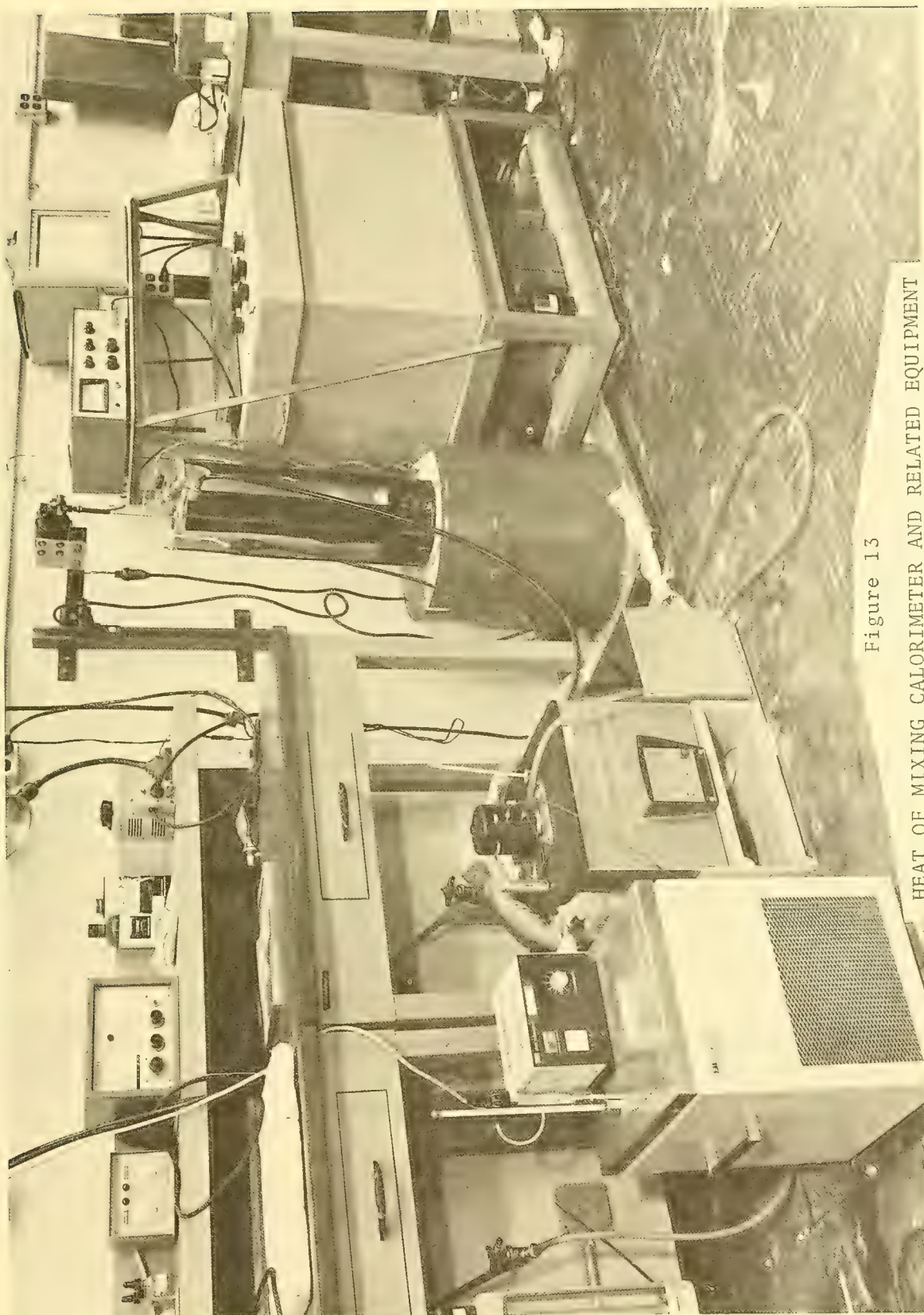


Figure 13
HEAT OF MIXING CALORIMETER AND RELATED EQUIPMENT

$$S^{\circ}/\text{oo} = 0.8996 + 28.29720 R_{15} + 12.80832 R_{15}^2 - 10.67869 R_{15}^3 + 5.98624 R_{15}^4 - 1.32311 R_{15}^5 \quad (5)$$

where R_t is the ratio of conductivity of sample water to that of t standard water having a salinity of exactly 35 $^{\circ}/\text{oo}$, both samples being at the same temperature, $t^{\circ}\text{C}$, and under a pressure of 1 atmosphere.

If measurements are made at a temperature other than 15°C , but not very far from 15°C , R_{15} may be computed by

$$R_{15} = R_t + 10^{-5} R_t (R_t - 1) (t - 15) [96.7 - 72.0 R_t + 37.3 R_t^2 - (0.63 + 0.21 R_t^2) (t - 15)] \quad (6)$$

Bissett Berman provides standard tables for direct evaluation of salinity from conductivity ratio and also for temperature corrections.

Theory

In developing a comprehensive theory for thermodynamic properties of sea water, two important questions arise. First, can sea water be treated as a two-component system? Our present knowledge and understanding of multicomponent electrolyte solutions is so limited that we are left with little choice but to consider sea salts as a single component. Fortunately, the relative proportions of major constituents of sea salts remain nearly constant (7) so that, to a first approximation, the ocean's salts may indeed be considered to be of a constant composition. Table 7 gives the composition of sea salts, based on Sverdrup's (8) composition of sea water. This permits us to treat sea salts as a single component with an apparent molecular weight of 62.83 (9).

The properties of sea water depend upon the concentration and the relative amounts of ions present. If we regard sea water as a binary mixture of sea salts and water, the enthalpy of the solution, H , is given by

$$H = x\phi L_S = x\bar{L}_S + (1-x)\bar{L}_W \quad (7)$$

Table 7

Composition of Sea Salts in Sea Water (8)
(assuming complete ionization)

<u>Ion</u>	<u>% of ions</u>
Cl^-	55.082
$\text{SO}_4^{=}$	7.691
HCO_3^-	0.406
Br^-	0.174
Na^+	30.646
Mg^{++}	3.686
Ca^{++}	1.161
K^+	1.103
Sr^{++}	0.029

Apparent Molecular Weight = 62.83

where,

ϕ_{LS} is the apparent enthalpy of the salts in solution
 $\bar{L}_S$ is the partial enthalpy of salts in solution
 $\bar{L}_W$ is the partial enthalpy of water in solution
 x is the mass fraction of salts in solution

In an attempt to develop mathematical expressions for the apparent and partial enthalpies, we are confronted with the second question: Is sea water solution dilute enough to permit the use of Debye-Hückel theory? At very dilute concentrations, enthalpies of electrolyte solutions may be calculated from Debye-Hückel theory, but deviations from this may become large as concentration increases. When mixtures of salts are involved, these deviations become significant at even lower concentrations. Once again our treatment is determined, not by what is precise and rigorous, but by expediency and limitations of knowledge. The Debye-Hückel theory has been slightly modified and extended by Bromley, as reported earlier (4). The pertinent equations, based on the extended Debye-Hückel theory are reproduced below:

$$\phi_{LS} = \frac{A_H}{2} \left(\frac{\sum m_i Z_i^2}{\sum m_i M_i} \right) I^{1/2} \left(\frac{1}{1+I^{1/2}} - \frac{\sigma I^{1/2}}{3} \right) - B'' \frac{\sum m_i}{2} - \frac{2}{n+1} C'' \left(\frac{\sum m_i}{2} \right)^n \quad (8)$$

$$\bar{L}_W = \frac{A_H}{2} \left(\frac{\sigma I^{1/2}}{3} \right) \left(\frac{2I^{3/2}}{1000} \right) + \frac{B''}{1000} \left(\frac{2\sum m_i M_i}{\sum m_i} \right) \left(\frac{\sum m_i}{2} \right) + \frac{2n}{n+1} \left(\frac{C''}{1000} \right) \left(\frac{2\sum m_i M_i}{\sum m_i} \right) \left(\frac{\sum m_i}{2} \right)^{n+1} \quad (9)$$

and,

$$\bar{L}_S = \frac{A_H}{2} \left(\frac{\sum m_i Z_i^2}{\sum m_i M_i} \right) \frac{I^{1/2}}{1+I^{1/2}} - 2B'' \frac{\sum m_i}{2} - 2C'' \left(\frac{\sum m_i}{2} \right)^n \quad (10)$$

The doubly primed constants are related (for 1-1) salts to

those of Lewis et al. (10) by:

$$\frac{B''}{dB/dT} = \frac{C''}{dC/dT} = 2.303RT^2 \left(\frac{\sum m_i}{\sum m_i M_i} \right) \left(\frac{4 \sum m_+ \sum m_-}{(\sum m_i)^2} \right) \quad (11)$$

B'' is also related to the constant B' used earlier in the heat-capacity equation by:

$$\frac{B''}{dB/dT} = \frac{B'}{\frac{2}{T} \frac{dB}{dT} + \frac{d^2 B}{dT^2}} \quad (12)$$

The calculated values of enthalpy change of mixing using these equations are in good agreement with the observed values for low salinity solutions. However, the deviations are relatively significant at higher concentrations. It is believed that these deviations can be reduced through use of a two-structure model which takes the concentrated solution behavior into account. Development and evaluation of such models is in progress; the details will be presented in a later publication.

Results

Relative Enthalpies: The relative enthalpies of sea salt solutions at 25°C and at 50°C have been reported earlier (2) and are reproduced in Tables 8 and 9.

The data at 73°C were correlated through the application of extended Debye-Hückel theory, as was done earlier for lower temperatures. Selected values of the observed and correlated heats of mixing are given in Table 10. The agreement appears to be good at lower salinities, though the deviations tend to increase with increasing salinity. It is hoped that a two structure model would provide a better fit of the data.

The values of C'' and n used in these calculations were -2.2359 and 1.5 respectively. The best value of B'' selected by the computer was 3.3296.

Table 11 gives the relative enthalpies of sea salt solutions at 73°, based on these computations. The corresponding partial and apparent enthalpies are given in Table 12.

Table 8

Sea Salt Solutions-Selected Values of
Relative Enthalpies at 25°C in Cal. per gram

Sea Salt Concen- tration, %	Apparent ϕL_∞ of Sea Salts	Partial L_∞ of Sea Salts	Partial L_∞ of Water	Enthalpy H of Solution
0	0	0	0	0
0.001	0.126	0.187	0.0000	0.0000
0.002	0.177	0.262	0.0000	0.0000
0.003	0.215	0.319	0.0000	0.0000
0.004	0.247	0.366	0.0000	0.0000
0.005	0.275	0.407	0.0000	0.0000
0.01	0.38	0.56	0.0000	0.0000
0.02	0.53	0.77	-0.0000	0.0001
0.03	0.63	0.92	-0.0001	0.0002
0.04	0.72	1.04	-0.0001	0.0003
0.05	0.80	1.14	-0.0002	0.0004
0.1	1.07	1.50	-0.0004	0.0011
0.2	1.39	1.90	-0.0010	0.0028
0.3	1.61	2.14	-0.0016	0.0048
0.4	1.76	2.29	-0.0021	0.0070
0.5	1.89	2.40	-0.0026	0.0094
1	2.20	2.54	-0.0035	0.022
2	2.30	2.17	+0.0026	0.046
3	2.15	1.53	0.019	0.064
4	1.90	0.82	0.045	0.076
5	1.60	0.10	0.079	0.080
6	1.27	-0.59	0.119	0.076
7	0.94	-1.25	0.165	0.066
8	0.60	-1.86	0.214	0.048
9	0.27	-2.41	0.265	0.024
10	-0.05	-2.91	0.317	-0.005
11	-0.36	-3.3	0.37	-0.040
12	-0.66	-3.7	0.41	-0.079

Table 9

Relative Enthalpy of Sea Salt Solutions at 50°

Salinity Percent	Apparent ϕL_s of sea salts cal/gm	Partial $\bar{L}_s$ of sea salts cal/gm	Partial $\bar{L}_w$ of water cal/gm	Enthalpy H, of solution cal/gm
0.	0.	0.	0.	0.
0.001	0.1801	0.2689	0.00000	0.00000
0.002	0.2532	0.3772	0.00000	0.00000
0.003	0.3087	0.4592	0.00000	0.00001
0.004	0.3551	0.5275	0.00000	0.00001
0.005	0.3957	0.5871	0.00000	0.00002
0.01	0.5522	0.8158	-0.00002	0.00006
0.02	0.7665	1.1254	-0.00006	0.00015
0.03	0.9255	1.3523	-0.00012	0.00028
0.04	1.0560	1.5368	-0.00018	0.00042
0.05	1.1683	1.6943	-0.00024	0.00059
0.1	1.5862	2.2687	-0.00068	0.00159
0.2	2.1190	2.9723	-0.00171	0.00424
0.3	2.4857	3.4350	-0.00286	0.00746
0.4	2.7686	3.7782	-0.00405	0.01107
0.5	2.9994	4.0479	-0.00527	0.01500
1.0	3.7559	4.8519	-0.01107	0.03756
2.0	4.4931	5.4570	-0.01967	0.08986
3.0	4.8583	5.6390	-0.02415	0.14575
4.0	5.0667	5.6824	-0.02565	0.20267
5.0	5.1954	5.6845	-0.02574	0.25977
6.0	5.2815	5.6907	-0.02612	0.31689
7.0	5.3459	5.7259	-0.02861	0.37421
8.0	5.4018	5.8061	-0.03515	0.43214
9.0	5.4583	5.9420	-0.04785	0.49124
10.0	5.5218	6.1421	-0.06891	0.55218
11.0	5.5976	6.4129	-0.10076	0.61574
12.0	5.6896	6.7603	-0.14600	0.68276

Table 10

Heats of Mixing of Sea Salt Solutions at 73°C

No.	<u>Dewar</u>		Weight, gms	<u>Pipet</u>		<u>Heats of Mixing, Cals</u>	
	Weight, gms	Salinity, %		Weight, gms	Salinity, %	Observed	Correlated
1.	3808.0	0	169.1	3.382		-31.983	-30.932
2.	3812.0	0.855	172.1	5.068		-20.678	-17.462
3.	3798.1	1.535	171.1	5.047		-12.183	-9.480
4.	3799.5	1.686	172.1	5.047		-10.034	-8.378
5.	3789.2	0	179.0	9.864		-108.124	-119.518
6.	3800.4	0.443	179.3	10.275		-78.890	-85.977
7.	3790.8	0	168.9	3.350		-31.857	-30.524
8.	3790.4	0.143	170.0	3.350		-22.836	-21.435
9.	3792.4	0.281	169.5	3.350		-19.807	-16.719
10.	3697.5	0.861	173.1	6.736		-34.955	-29.758
11.	3700.5	1.124	173.2	6.736		-27.718	-24.767
12.	3703.7	1.375	173.8	6.736		-22.554	-21.077
13.	3799.7	1.832	174.5	6.735		-18.546	-15.962
14.	3790.1	0.671	172.4	5.118		-27.022	-21.208

Table 11

Relative Enthalpies of Sea Salt Solutions at 73°C, Cals/gm

Salinity, %	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.	0.0022	0.0059	0.0104	0.0156	0.0212	0.0273	0.0338	0.0405	0.0475
1.	0.0547	0.0622	0.0699	0.0777	0.0858	0.0939	0.1023	0.1107	0.1194	0.1281
2.	0.137	0.146	0.155	0.164	0.174	0.183	0.192	0.202	0.212	0.221
3.	0.231	0.241	0.251	0.261	0.271	0.282	0.292	0.302	0.313	0.323
4.	0.334	0.344	0.355	0.366	0.377	0.387	0.398	0.409	0.421	0.432
5.	0.443	0.454	0.465	0.477	0.488	0.500	0.511	0.523	0.535	0.547
6.	0.558	0.570	0.582	0.594	0.606	0.619	0.631	0.643	0.656	0.668
7.	0.680	0.693	0.706	0.718	0.731	0.744	0.757	0.769	0.783	0.796
8.	0.809	0.822	0.836	0.849	0.863	0.876	0.890	0.904	0.917	0.931
9.	0.945	0.959	0.973	0.987	1.002	1.016	1.030	1.045	1.060	1.074
10.	1.089	1.104	1.119	1.134	1.149	1.164	1.180	1.195	1.211	1.226
11.	1.242	1.258	1.274	1.290	1.306	1.322	1.338	1.355	1.371	1.388
12.	1.405	1.421	1.438	1.455	1.473	1.490	1.507	1.525	1.543	1.560

Table 12

Partial and Apparent Enthalpies of Sea Salt Solutions

at 73°C

Salinity, %	Apparent ϕL_S of sea salts Cals/gm	Partial $\bar{L}_S$ of sea salts Cals/gm	Partial $\bar{L}_W$ of water Cals/gm	Enthalpy H of solution Cals/gm
0	0	0	0	0
0.001	0.2435	0.3637	0.00000	0.00000
0.002	0.3425	0.5108	0.00000	0.00001
0.003	0.4178	0.6222	-0.00001	0.00001
0.004	0.4809	0.7153	-0.00001	0.00002
0.005	0.5361	0.7966	-0.00001	0.00003
0.01	0.7494	1.1095	-0.00003	0.00008
0.02	1.0429	1.5358	-0.00010	0.00021
0.03	1.2618	1.8507	-0.00018	0.00038
0.04	1.4422	2.1082	-0.00026	0.00058
0.05	1.5981	2.3292	-0.00038	0.00080
0.1	2.1832	3.1464	-0.00096	0.00218
0.2	2.9441	4.1787	-0.00247	0.00589
0.3	3.4803	4.8843	-0.00422	0.01044
0.4	3.9030	5.4275	-0.00612	0.01561
0.5	4.2550	5.8705	-0.00812	0.02128
1.0	5.4739	7.3386	-0.01884	0.05474
2.0	6.8486	8.8774	-0.04140	0.13697
3.0	7.7060	9.8023	-0.06484	0.23118
4.0	8.3401	10.5059	-0.09024	0.33361
5.0	8.8567	11.1238	-0.11932	0.44284
6.0	9.3069	11.7179	-0.15402	0.55842
7.0	9.7198	12.3297	-0.19645	0.68039
8.0	10.1137	12.9757	-0.24887	0.80910
9.0	10.5010	13.6732	-0.31373	0.94509
10.0	10.8909	14.4336	-0.39363	1.08909
11.0	11.2903	15.2662	-0.49140	1.24194
12.0	11.7048	16.1786	-0.61006	1.40458

Since a new model is being worked upon, some minor revisions are likely; hence the results are necessarily preliminary in nature.

Comparison with heat capacity data: An estimate of the relative enthalpies may also be obtained from the heat capacity data of Bromley et al. (1). In the temperature range involved, the heat capacity of sea water is given by:

$$C_P = C_{P_W}^* (1-x) + x(\phi C_{P_S}) \quad (13)$$

$$\begin{aligned} (\phi C_{P_S}) = \overline{C}_{P_S}^{\circ} + \frac{A_j}{2} \left(\frac{\sum m_i Z_i^2}{\sum m_i M_i} \right) I^{1/2} \left(\frac{1}{1+I^{1/2}} - \frac{\sigma I^{1/2}}{3} \right) \\ - B' \frac{\sum m_i}{2} \end{aligned} \quad (14)$$

where,

$$\begin{aligned} A_j = 7.858661 + 0.04424799t + (0.2129136 \times 10^{-2})t^2 \\ - (0.1837382 \times 10^{-4})t^3 + (0.7077757 \times 10^{-7})t^4 \end{aligned} \quad (15)$$

and

$$\begin{aligned} B' = (272)(0.171253 \times 10^{39})T^{-17} - 0.072070739 \\ + (1.05884208 \times 10^{-4})T \end{aligned} \quad (16)$$

$\overline{C}_{P_S}^{\circ}$ is a sixth degree polynomial in t which cancels while evaluating relative enthalpies.

The relative enthalpy at any temperature, $(RH)^t$ is given by

$$\begin{aligned} (RH)^t - (RH)^{25} &= \int_{25}^t \{C_P - C_{P_W}^* (1-x) - \overline{C}_{P_S}^{\circ} x\} dt \\ &= \int_{25}^t (\phi C_{P_S} - \overline{C}_{P_S}^{\circ}) x dt \end{aligned}$$

$$= x \cdot \frac{1}{2} \left(\frac{\sum m_i Z_i^2}{\sum m_i M_i} \right)^{1/2} \left(\frac{1}{1+I^{1/2}} - \frac{\sigma I^{1/2}}{3} \right).$$

$$\int_{25}^t A_j dt - x \frac{\sum m_i}{2} \int_{25}^t B' dt \quad (17)$$

which can conveniently be evaluated.

These calculated values are compared with the observed values in Table 13. Again, the agreement is good at low salinities, with slight deviations at higher salinities.

Table 13

Comparison of Relative Enthalpy of Sea Salt Solutions at 73°C

<u>Salinity, %</u>	<u>Enthalpy of solution, H, Cals/gm</u>	
	<u>(observed)</u>	<u>(Calculated from heat capacity data)</u>
1	.055	.055
2	.137	.138
3	.231	.231
4	.334	.333
5	.443	.440
6	.558	.552
7	.680	.671
8	.809	.795
9	.945	.926
10	1.089	1.063
11	1.242	1.208
12	1.405	1.363

The constant B'' may also be evaluated from heat capacity data, as done previously (2). Equations 12 and 16 may be combined to yield

$$B'' = 17 \times 0.171253 \times 10^{39} \times T^{-16} - 0.072070739 \times T + 0.52942104 \times 10^{-6} \times T^2 + 22.13673 \quad (18)$$

Table 14 gives the values of B'' obtained from heat capacity and heat of mixing data. The agreement is good.

Table 14

Observed and Calculated Values of B''

<u>Temperature, °C</u>	<u>B''</u>	
	<u>Observed</u>	<u>Calculated</u>
25	6.0993	6.0993
50	4.5254	4.5800
73	3.3296	3.5811

Comparison with Connors' data: Some data on heats of mixing of sea water solutions has also been reported by Connors (11) in the temperature range 0 to 30°C and salinity range 10‰ to 40‰. Although most of Connors' data is at 2°C and a precise comparison will have to await our low temperature measurements, a fair comparison may be made by using equation (18) for B'' in the extended Debye-Hückel correlation. Connors' observed temperature changes were converted to heats of mixing and compared with our estimated values, as shown in Table 15. The two values agree within his error estimates.

BOILING POINT ELEVATION(BPE)

Boiling point elevation data is required for design of desalination plants. In case of multi-effect or multi-stage flash evaporators, the data is required for calculation of heat transfer areas and rates. In case of reverse osmotic

Table 15
Comparison with Connors' (11) Data

<u>Temperature</u> °C	<u>Solution 1</u>		<u>Solution 2</u>		<u>Heat of Mixing, Cals.</u>	
	<u>Salinity</u> 0/00	<u>Weight</u> gms	<u>Salinity</u> 0/00	<u>Weight</u> gms	<u>Observed</u> (Connors)	<u>Estimated</u> (From our data)
25.3	10.24	0.5	60.50	0.5	.024	.022
24.6	10.24	0.5	60.50	0.5	.024	.023
21.4	10.24	0.5	60.50	0.5	.027	.027
20.0	10.24	0.5	60.50	0.5	.028	.028
15.0	10.24	0.5	60.50	0.5	.035	.035
14.2	10.24	0.5	60.50	0.5	.036	.037
9.15	10.24	0.5	60.50	0.5	.047	.045
3.10	10.24	0.5	60.50	0.5	.063	.057
2.75	10.24	0.5	60.50	0.5	.065	.058
2.00	10.24	0.5	60.50	0.5	.064	.060

processes, this data may be used to calculate basic thermodynamic quantities of solution necessary for design. BPE can also be used to check other experimentally obtained data or presently available semi-empirical and empirical expressions for mixed electrolytes like sea water. Boiling point elevation data for actual sea water is also important because there has been no experimental determination other than the present work. All the previous estimations have been based on NaCl or synthetic sea water. The objective of this work was to obtain data for boiling point elevation of sea water at various concentrations and temperatures at relatively short intervals of concentration and temperature which would be useful in obtaining accurate correlations and in testing previously existing correlations. It appears that there is a large discrepancy in the values predicted by currently available correlations. In order to obtain these data, the apparatus, the development of which was previously described (2), was used. See Figure 15. The items from left to right are a nitrogen cylinder, ballast drum with pressure controls and heater controls beneath the boiling point apparatus proper. At the right is the recorder, with controls, quartz thermometer, digital analogue converter, and potentiometer beneath. Since the range of this apparatus is limited in pressure, a new apparatus (Figure 16) has been designed and built and is now being tested. The experimental data obtained so far with natural sea water encompass a concentration of from 0 to twice normal concentration, and a temperature range of 80° to 120°C.

Experimental Procedure, Old Apparatus

Equipment: A few minor but critical changes have been made of the apparatus previously described (2). These modifications include changes of some glass parts with metal parts to enable operation at higher pressures, incorporation of a flow-through sampler, and change of gasket material.

Operation:

Solution Preparation - The sea water used in this work was obtained through the Scripps Institution of Oceanography, La Jolla, California. The Pacific Ocean water, from about 800 feet off-shore, is pumped from a point midway between the ocean floor and ocean surface (about 6' from the surface), collected and delivered in 20 liter plastic bottles. The pH of the sea water is

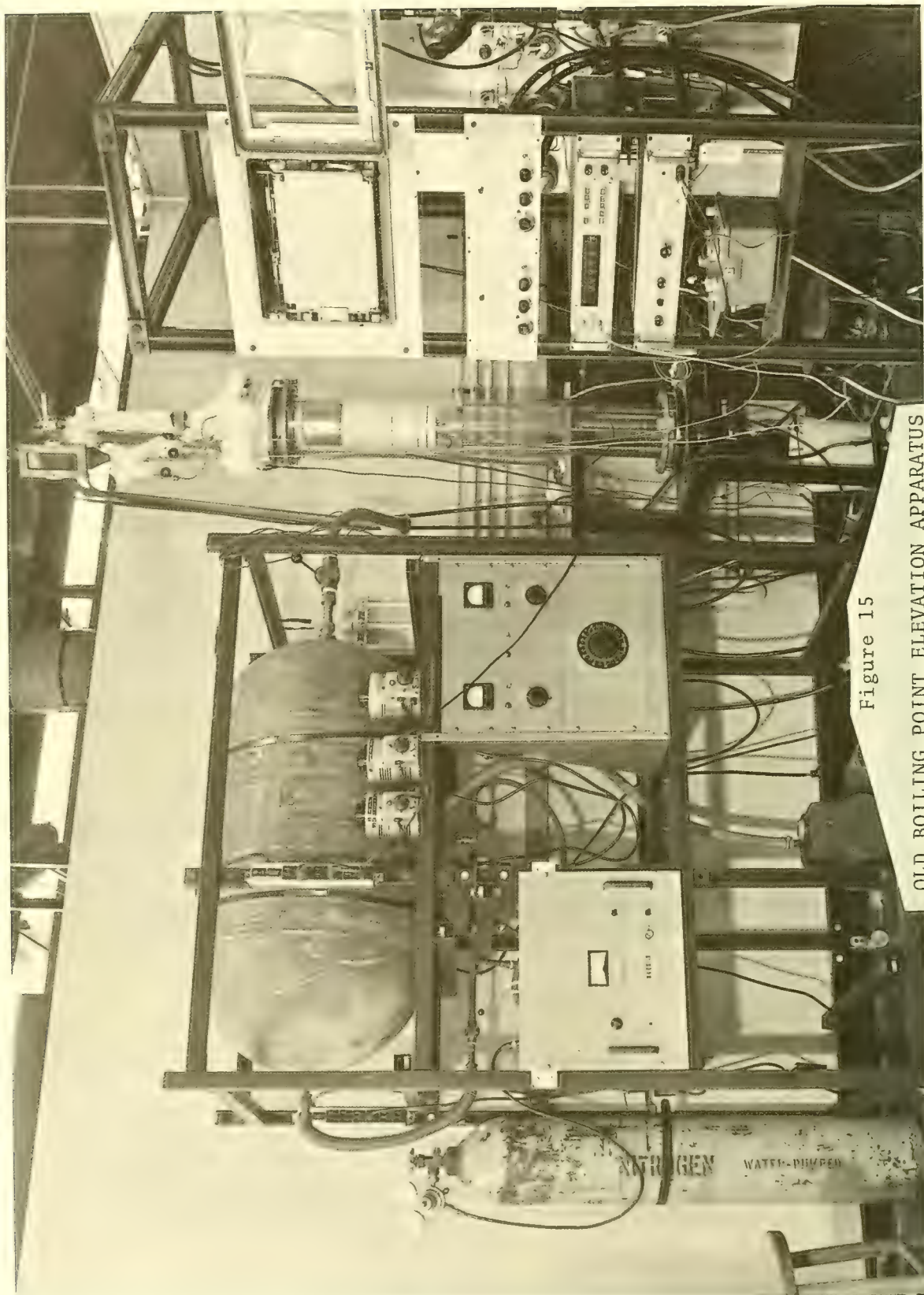


Figure 15
OLD BOILING POINT ELEVATION APPARATUS

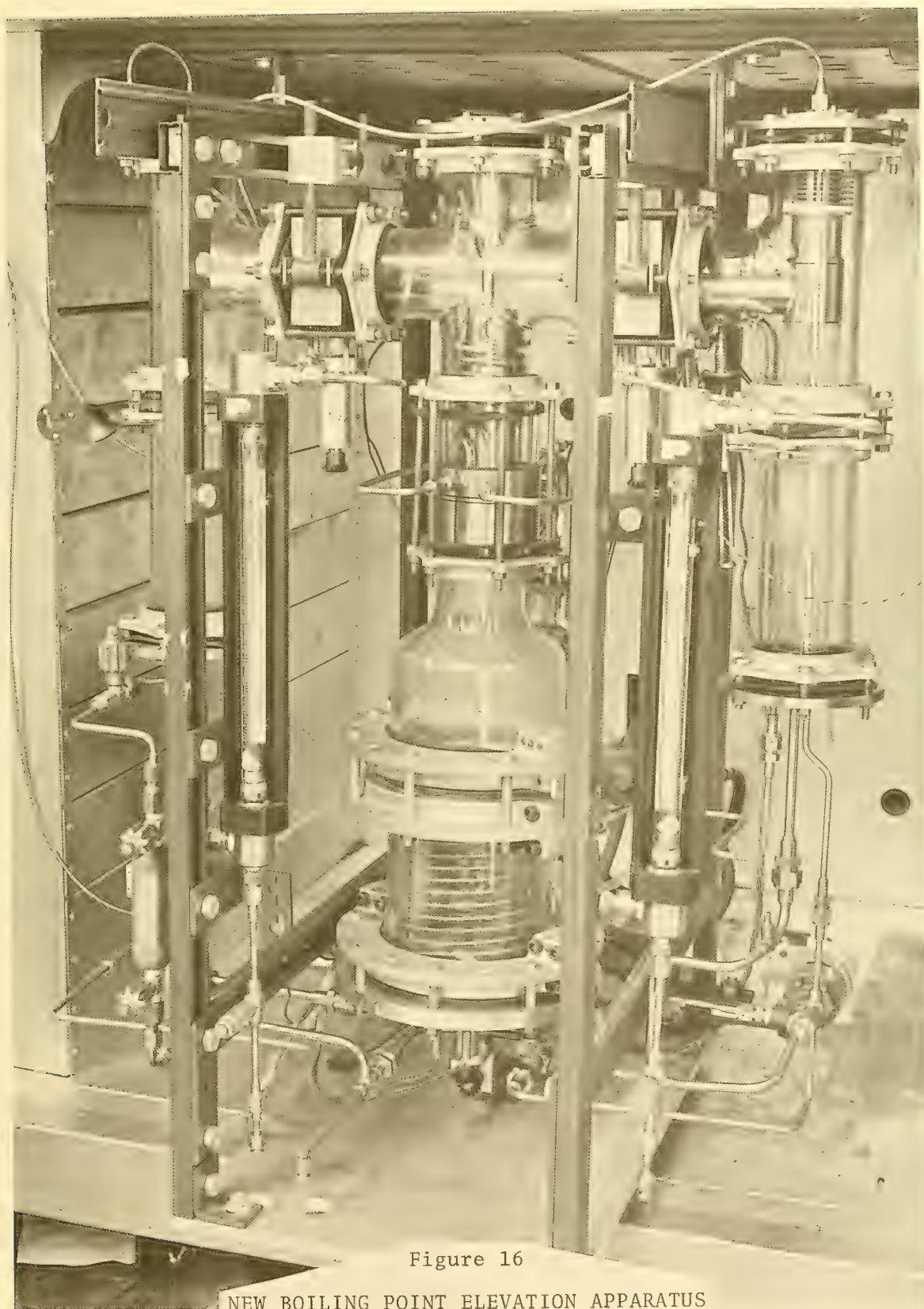


Figure 16

NEW BOILING POINT ELEVATION APPARATUS

about 8.2.

The bicarbonate ions are removed by adding concentrated sulfuric acid to the original sea water, to reduce the pH to about 4.5 (about 3.2 ml of conc. sulfuric acid, specific gravity 1.84, are required for 45 liters of sea water). A batch of about 40 liters is prepared for each concentration and kept in a 50-liter polyethylene bottle. The solution for a run is drawn from these bottles. Each run required about 13 liters of solution.

Concentrates of sea water are prepared by boiling the acidified sea water at atmospheric pressure to the required concentration and stored. It was found that the pH of the acidified solution did not change appreciably during concentration.

The procedure described below is used for runs of distilled water as well as the sea water solutions. (No samples are taken in the case of distilled water.) A run of distilled water is made once after two runs of sea water. This is necessary to check the calibration at each pressure.

Start up - The condenser water is first turned on. Then the solution (or distilled water) is sucked into the ebulliometer, through the charge-discharge tube, to a height of 25". The main heaters are then switched on and the solution allowed to boil. In about one hour, vapor rises to the condenser and starts to condense. Tape heaters around the aluminum cylinder and the vapor tube are switched on. Valves on the condensate lines are kept open. About 20 minutes later, the first drops of condensate start coming down through the ports indicating that the condensate reservoirs are full. Now the heaters in these reservoirs are switched on.

Recording temperatures - The pressure is brought to the desired value by putting the pressure controller on control mode (with vacuum pump on and nitrogen line pressure 55 psig), and changing the set point to the desired value. About 20 minutes are required for equilibration. During this time the condensate temperature is monitored to ensure equilibrium.

When the condensate temperature is steady, the calibration of the temperature probes for the particular pressure is started. Temperatures T1, T2, and T1-T2 are

observed with boiling condensate flowing on both probes. T1 and T2 should be the same during solution runs and distilled water runs. If they do not correspond, the boiling is stopped, and the ebulliometer is checked for possible malfunctions. The difference, T1-T2, indicates the correction to be applied to the T1-T2 observed when the solution is flowing on the probe.

Temperatures are recorded for at least half an hour. Then the valve on the condensate line to the solution temperature probe is closed, the pump heater is switched on, and the power adjusted. The condensate supply reservoir to solution port is still full. The heater in it is kept on for some time after the flow into the reservoir is stopped so that condensate does not spill over and dilute the solution on the probe. The system requires about 15 minutes to reach equilibrium after the pump is started. The sampler line is opened when a steady flow is obtained. T1, T2 and T1-T2 are recorded when circulation is maintained.

Sampling procedure - First, the sampler is filled with fresh solution and put in place on the ebulliometer. When the pump maintains a steady flow, the valves are opened and care is taken to remove all air bubbles in the sample line. With the continuous flow, the temperatures are observed. When T1-T2 remains steady for a satisfactory length of time (about half an hour), the valves are closed. The sampler is taken out and cooled to room temperature. The flange and coupling ends are taken out and the exterior of the sampler is washed and dried thoroughly. This is done to prevent any contamination of the sample. The dry ends are put back on the valves and the valves opened slowly so that the sample reaches atmospheric pressure. Then the contents are emptied into a clean dry flask and labelled. The sampler is put back on the ebulliometer with fresh solution.

Once the set of readings for one pressure and samples have been taken, the pressure is changed to the next desired value and the procedure continued.

Analysis - In the initial stages, the samples were analyzed by the Knudsen method (12), i.e. titration with silver nitrate solution in standard equipment. This has an accuracy of ± 0.02 0/00 in chlorinity or salinity. In the later stages a Bissett-Berman, Model 6230, Inductive Salinometer was used. The accuracy is claimed to be ± 0.005 parts per thousand (0/00) in salinity.

Since the range is limited in both cases, samples with concentrations outside the range (larger in both cases) were diluted with distilled water, by weight, to normal concentrations. Then the chlorinity or salinity was determined.

Ranges: Knudsen method, Salinity: 29 ‰ to 39 ‰
Salinometer, Salinity: 4 ‰ to 51 ‰

The determinations of concentrations have to be done very carefully, since the boiling point elevation is determined with an accuracy of $\pm 0.001^{\circ}\text{C}$. The corresponding accuracy in concentration determination is approximately 0.1%. A test run was made in order to determine the effects of acidification, boiling, concentration, and redilution of concentrated sea water, on the determination of salinity by salinometer. The results showed that the processes do not affect the salinity determination appreciably and no correction is required.

Limitations of the Old Apparatus: The old apparatus has been used so far to determine the BPE of sea water between 80°C and 120°C . Since the body of the apparatus is made of glass it cannot be used at higher pressures or temperatures. Also at higher temperatures, the problem of heat loss becomes more acute, requiring high capacity heaters in the condensate collecting bowls. In the lower temperature and pressure range, the efficiency of the Cottrell pumps fall, and this makes pressure control difficult.

New Apparatus

Design: For reasons described above, the old apparatus is unsuitable below 80°C or above 120°C . In order to obtain data outside this range, construction of a new apparatus was essential. In order that this new apparatus (Figure 17) withstands higher pressure, it has been made smaller, but with sturdier glass which can be easily replaced by stainless steel if required. The Cottrell pumps have been replaced by centrifugal pumps, so that the operation does not become troublesome at lower pressures. In order to prevent the complication arising due to heat loss, the whole apparatus is enclosed in a temperature-controlled oven, which is kept at a temperature slightly lower than the boiling point of pure water. The rest of the design was done in such a way as to avoid the problems encountered in the operations of the old BPE apparatus. Only modifications are being made to improve

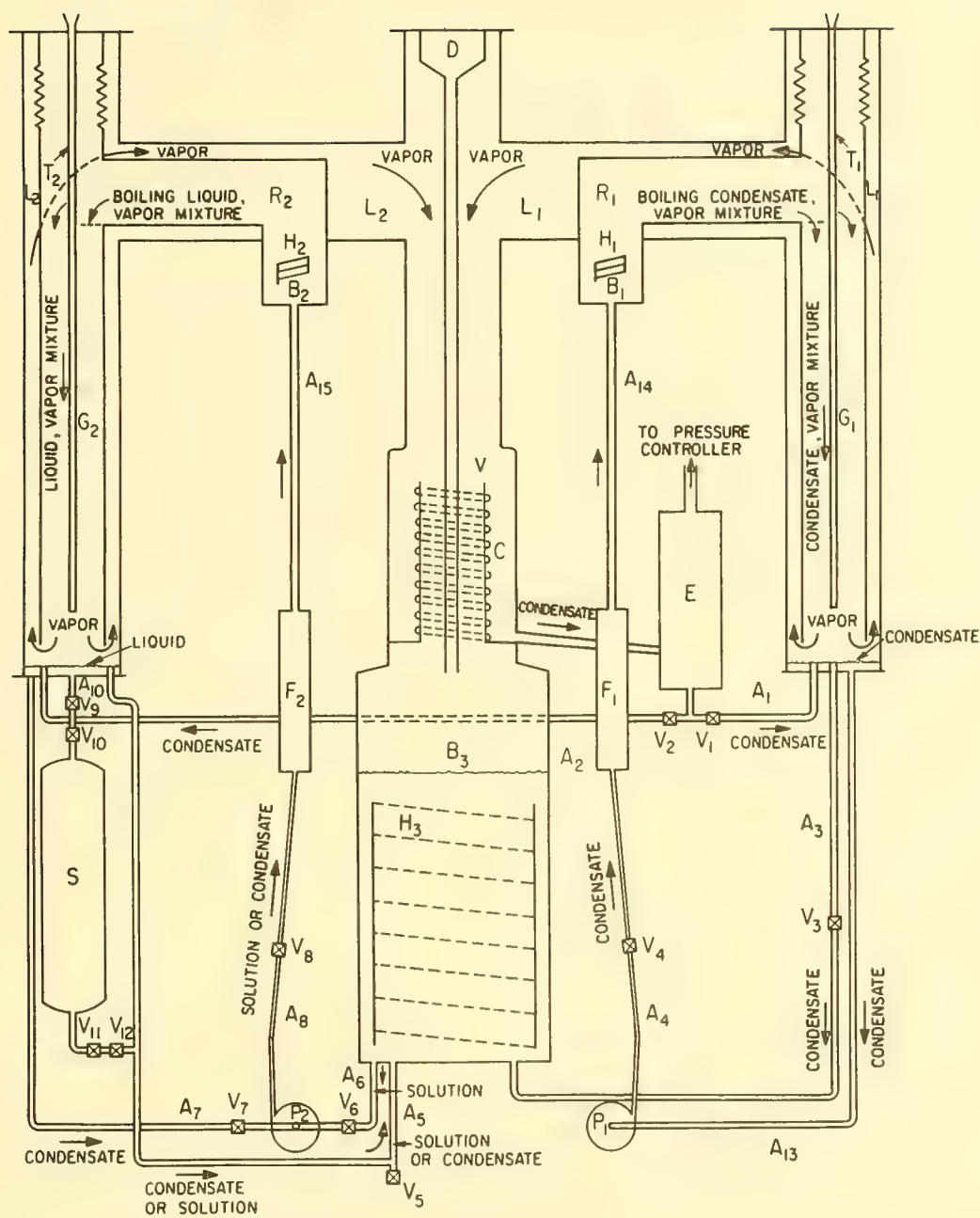


Figure 17

NEW BOILING POINT APPARATUS - SCHEMATIC

the operating characteristics based on partial tests completed. The new apparatus is working fairly well.

Description of the New Apparatus: The apparatus consists of a main boiler, B₃, in which the test solution is boiled by a 2 Kw wire heater, H₃. Approximate capacity of B₃ is 3.5 liters. Vapor rises through the central tube of condenser C, into the vapor space V, then passes downward into condenser C, where it condenses, and then collects in the condensate collector, E. The top of the condensate collector is connected to the pressure controller. The condensate from the collector can be channeled to either or both of the thermometer legs, L₁ or L₂, through tubes A₁ and A₂ and valves V₁ and V₂. For normal mode of operation, V₂ is closed and condensate flows into L₁ and then through tubes A₁₃ (to pump P₁) and A₃ (through valve V₃ to the main boiler, B₃). Usually a small liquid head is maintained over the bottom plate of leg L₁, so that the pump, P₁, remains primed. P₁ pumps the condensate through flowmeter, F₁, into preboiler, B₁, fitted with heater, H₁ (200 watts). Thermometer, T₁, is inside a housing, G₁, which is inside leg L₁. The vapor and boiling condensate mixture falls along the inside of G₁, and separates at the bottom. The vapor passes up through the annular space outside G₁, into vapor space V, and then into condenser C. The condensate mixes with the condensate coming from E. On the other side, with valve V₇ closed, boiling solution from B₃ is pumped by P₂ through flowmeter F₂, through preboiler B₂ (fitted with heater H₂, as in case of preboiler B₁). The mixture of boiling solution and vapor passes through passage R₂, along the thermometer T₂, inside G₂. At the bottom, the vapor solution mixture separates. The vapor flows back to the condenser in a manner similar to that of the vapor from leg L₁. The solution accumulating at the bottom of L₂ passes through sampler S, and overflow tube A₅, into main boiler B₃. The sampler can be withdrawn from line after some time, without disturbing the system, by closing the valves V₉, V₁₀, V₁₁ and V₁₂. When it is required to calibrate the equipment by running boiling condensate on both the thermometers simultaneously, the valves V₂ and V₇ are opened, and V₆, V₉, V₁₀, V₁₁, V₁₂ closed. Then the configuration of the leg L₂ becomes exactly similar to the configuration of the leg L₁ and they operate in the same way. The valves V₄ and V₈ are used to control the liquid flow rate over the thermometers. The valve V₅ is used for draining the system.

Results

BPE's over temperature range from about 80°C to 120°C at different concentrations are listed in Tables 17-23. The concentrations in the case of normal sea water (3.47% Table 18) and twice concentrated sea water (6.59%, Table 21) were determined by the Knudsen method. The observed BPE values were fitted to a second degree polynomial (Equation 20) by the method of least squares. The constants of the fits are shown in Table 16, along with the standard deviation σ . The smoothed BPE values are shown along with observed values in Table 24.

No attempt has been made to fit the data obtained to a polynomial in salinity since further data at different concentrations are required. The observed boiling point elevation values have been plotted as functions of salinity with condensate boiling point (t_o) as parameter, in Figure 18. Figure 19 shows BPE's as a function of temperature, salinity being the parameter.

Osmotic coefficients (ϕ) and activities of water in the solutions were computed. Table 25 gives values of activities of water in the sea water solutions. Table 26 and Figure 20 show values of osmotic coefficients. Activity coefficients of solute have not yet been evaluated in this study because of the limited data obtained so far.

Table 27 gives the values of osmotic pressures of solution computed at 80 and 100°C. Partial molal volumes ($\bar{V}_s$) of water in NaCl solutions, taken from Stoughton and Lietzke (13) were assumed to hold for sea salt solutions also. The osmotic pressures were evaluated according to the formula

$$\pi = \frac{M_s RT \phi}{\bar{V}_s (1000)} \sum m_i \quad (19)$$

using the actual salinities reported in Tables 17 to 22. The salinities reported in Tables 16 and 24-27 are only nominal values. Actual values should be used for computation of any derived quantity like activity.

Equation used for smoothing boiling point elevation data over temperature range 80-105°C is:

$$\theta = a + bt + ct^2 \quad (20)$$

where,

θ = boiling point elevation, °C
 t = condensate boiling point °C
 a, b, c = constants of fit, given in Table 16

Table 16

Values of Constants of Equation 20 (Preliminary Values)

<u>Salinity*</u> <u>wt %</u>	<u>a</u>	<u>b x 10³</u>	<u>c x 10⁶</u>	<u>σ deg C</u>
1.70	0.1780	-0.1286	8.5714	0.0001
3.47	0.2852	1.4593	9.2857	0.0005
5.05	0.4371	2.1636	13.5714	0.0002
6.59	0.4132	6.7743	-2.8571	0.0002

* Nominal concentration

Discussion

The sulfuric acid added to the sea water for removal of bicarbonate ions changes the salinity by 1 part in 3000. This does not change the BPE in the range of accuracies used in this work.

Boiling point elevation depends on the activity of water in the solution. As the concentration of solution

Table 17

BPE of Half Normal Sea Water, Nominal Conc. 1.70% by Weight

<u>Temperature</u> <u>°C</u>	<u>Run No.</u>	<u>Salinity *</u> <u>wt %</u>	<u>BPE</u> <u>°C</u>
85.0	2A	1.6967	0.228
"	2B	1.6986	0.230
90.0	2A	1.7038	0.236
"	2B	1.7003	0.235
"	2C	1.7064	0.236
95.0	2A	1.7111	0.244
"	2B	1.7079	0.245
"	1A	1.7045	0.243
"	1B	1.7066	0.243
100.0	2A	1.7117	0.252
"	2B	1.7127	0.252
"	1A	1.7133	0.251
"	1B	1.7075	0.251
105.0	2A	1.725	0.263
"	2B	1.720	0.263

*Salinities determined with salinometer measurements.

Table 18

BPE of Normal Sea Water, Nominal Conc. 3.47% by Weight

<u>Temperature</u> °C	<u>Run No.</u>	<u>Salinity *</u> wt%	<u>BPE</u> °C
80.0	1A	3.467	0.261
"	1B	3.469	0.461
85.0	1A	3.470	0.477
"	1B	3.472	0.477
90.0	1A	3.474	0.492
"	1B	3.470	0.492
95.0	1A	3.472	0.507
"	1B	3.472	0.507
100.0	1A	3.474	0.524
"	1B	3.472	0.524
105.0	1A	3.476	0.541
"	1B	3.488	0.542

*Salinities determined using the Knudsen method.

Table 19

BPE of Normal Sea Water, Nominal Conc. 3.35% by Weight

<u>Temperature</u> <u>°C</u>	<u>Run No.</u>	<u>Salinity*</u> <u>wt %</u>	<u>BPE</u> <u>°C</u>
80	4A	3.3528	0.447
90	4A	3.3560	0.475
100	4A	3.3527	0.505
100	4B	3.3552	0.505
110	4A	3.3570	0.536
110	4B	3.3585	0.536
120	4A	3.3534	0.568

*Salinity determined with salinometer.

Table 20

BPE of One and One-Half Times Normal Sea Water,
Nominal Conc. 5.05% by Weight

<u>Temperature</u> °C	<u>Run No.</u>	<u>Salinity*</u> wt %	<u>BPE</u> °C
80.0	1A	5.0436	0.697
"	1B	5.0362	0.696
85.0	1A	5.0458	0.719
"	1B	5.0429	0.719
90.0	1A	5.0524	0.742
"	1B	5.0493	0.742
95.0	1A	5.0548	0.766
"	1B	5.0326	0.762
100.0	1A	5.0648	0.790
"	1B	5.0555	0.789
105.0	1A	5.0638	0.814
"	1B	5.0599	0.814

*Salinity determined with salinometer.

Table 21

BPE of Twice Normal Sea Water, Nominal Conc. 6.59% by Weight

<u>Temperature</u> <u>°C</u>	<u>Run No.</u>	<u>Salinity*</u> <u>wt %</u>	<u>BPE</u> <u>°C</u>
80.0	2A	6.571	0.937
"	2B	6.575	0.936
85.0	2A	6.679	0.968
"	2B	6.611	0.968
90.0	2A	6.571	0.998
"	2B	6.604	1.000
95.0	2A	6.595	1.030
"	2B	6.590	1.032
100.0	2A	6.624	1.062
"	2B	6.619	1.062
105.0	2A	6.591	1.093
"	2B	6.579	1.093

*Salinity determined by Knudsen method. (Probably over-
estimation by 0.3 to 0.5% of the value)

Table 22

BPE of Twice Normal Sea Water, Nominal Conc. 6.70% by Weight

<u>Temperature</u> °C	<u>Run No.</u>	<u>Salinity*</u> wt %	<u>BPE</u> °C
85.0	4A	6.6789	0.992
90.0	4A	6.7173	1.023
"	4B	6.7224	1.024
100.0	4A	6.7165	1.088
"	4B	6.7369	1.090

*Salinity determined with salinometer.

Table 23

BPE of Twice Normal Sea Water, Nominal Conc. 6.58% by Weight

<u>Temperature</u> °C	<u>Salinity*</u> wt %	<u>BPE</u> °C
120	6.5937	1.192
110	6.5872	1.124
100	6.5884	1.061
90	6.5786	0.998

*Salinity determined with salinometer.

Table 24

Boiling Point Elevation of Sea Salt Solutions (°C)

Salinity* wt % →	1.70		3.47		5.05		6.59		6.70	
	Observed	Smooth	Observed	Smooth	Observed	Smooth	Observed	Smooth	Observed	Smooth
t _o ↓										
80.0	-	-	0.461	0.461	0.697	0.697	0.937	0.937		
85.0	0.229	0.229	0.477	0.476	0.719	0.719	0.968	0.968	0.992	
90.0	0.236	0.236	0.492	0.492	0.742	0.742	1.000	1.000	1.023	
95.0	0.243	0.243	0.507	0.508	0.765	0.765	1.031	1.031		
100.0	0.251	0.251	0.524	0.524	0.789	0.789	1.062	1.062	1.088	
105.0	0.259	0.259	0.541	0.541	0.814	0.814	1.093	1.093		

t_o = Condensate Boiling Point (°C)

* Nominal Concentrations. For actual concentrations see Tables 17-22.

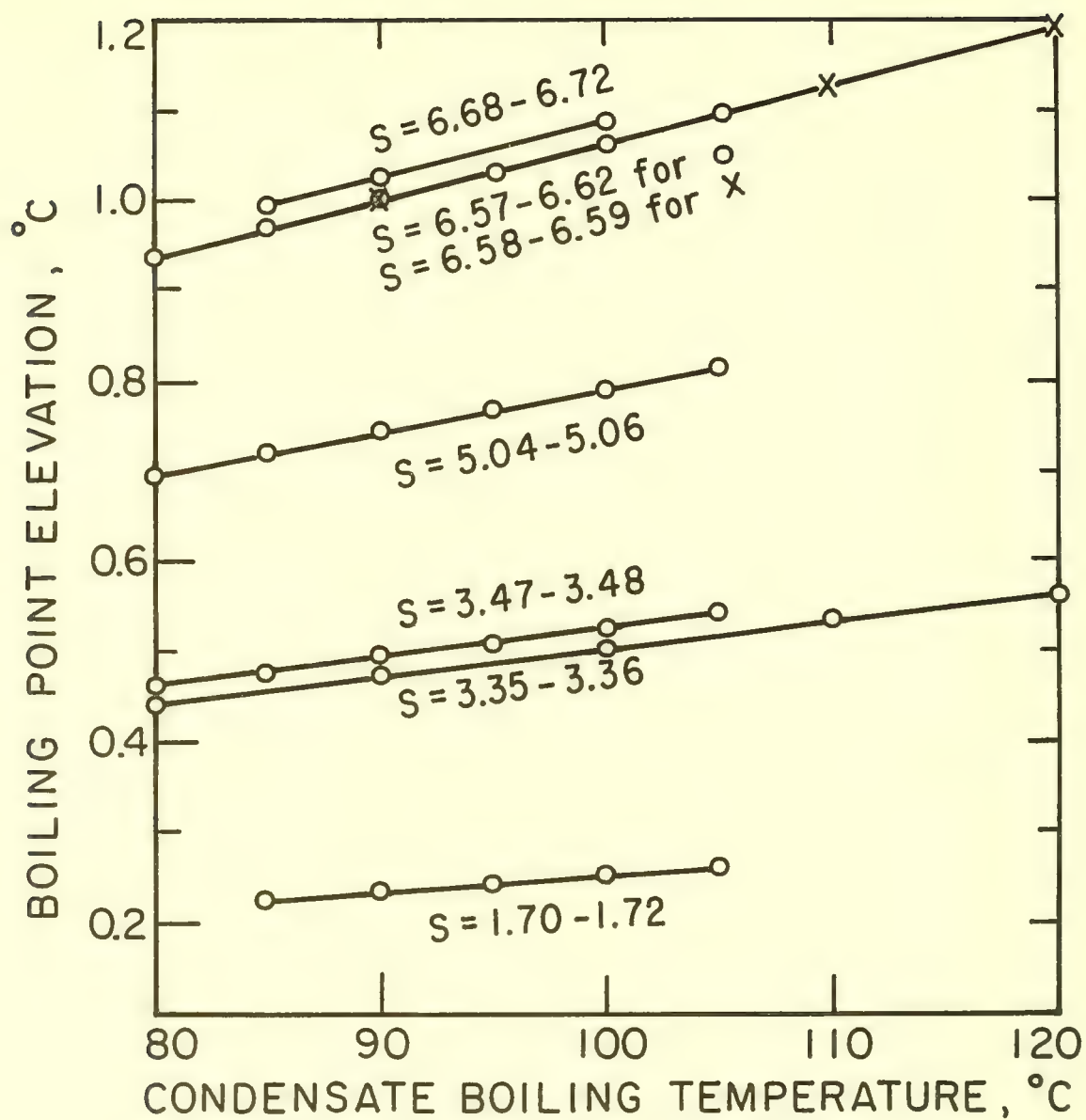


Figure 18

BPE VS. CONDENSATE BOILING POINT

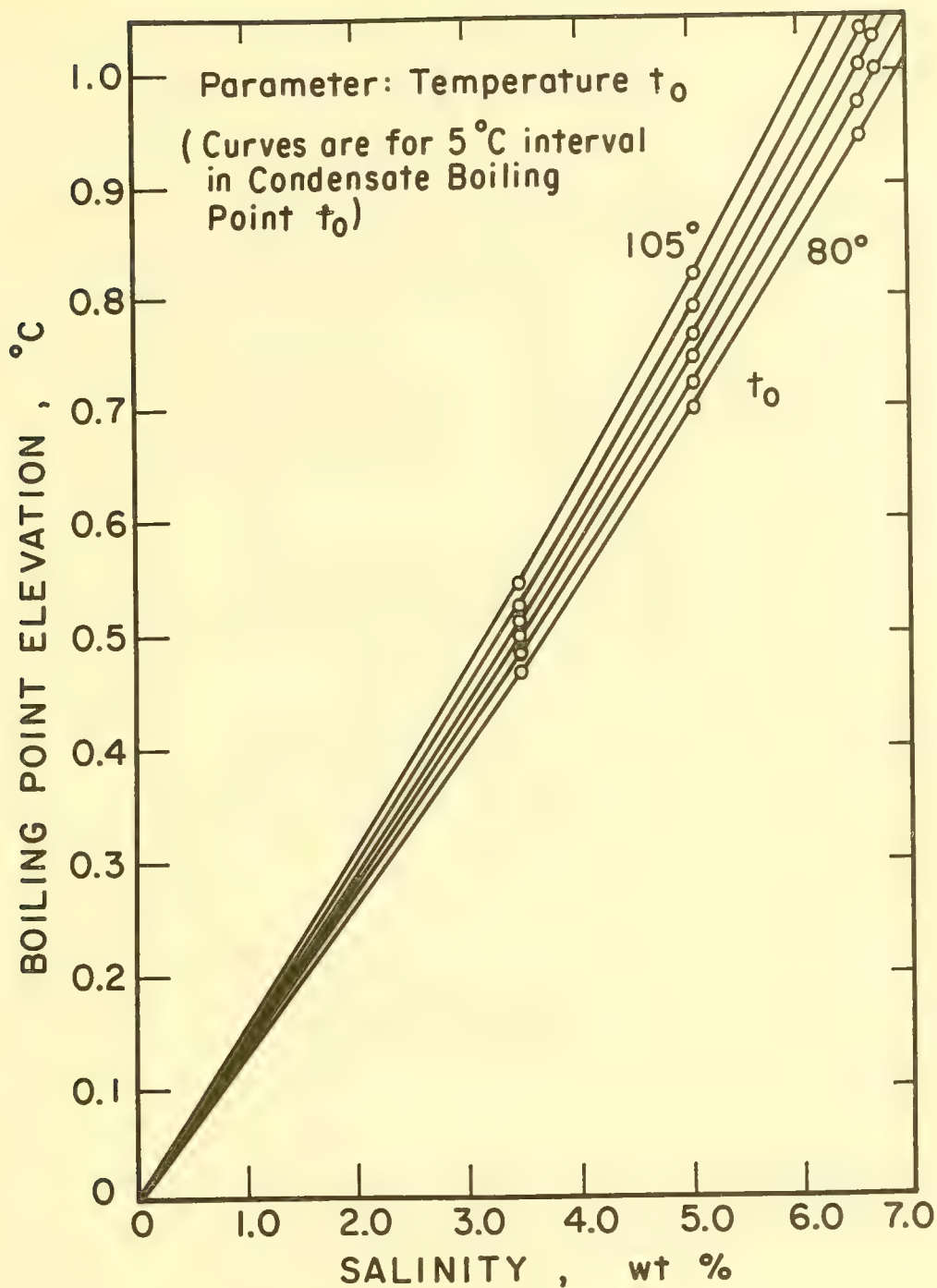


Figure 19

BPE VS. SALINITY, PARAMETER: TEMPERATURE t_0

Table 25

Activities of Water in Sea Water Solutions (computed)

Temp. T _O °C	Pressure in. Hg	Salinity, wt%				
		1.70	3.47	5.05	6.59	6.70
80.0	13.985	-	0.9818	0.9726	0.9635	-
85.0	17.070	0.9913	0.9818	0.9727	0.9635	0.9627
90.0	20.703	0.9913	0.9818	0.9728	0.9636	0.9627
95.0	24.961	0.9912	0.9819	0.9729	0.9637	-
100.0	29.921	0.9912	0.9819	0.9729	0.9638	0.9630
105.0	35.672	0.9912	0.9819	0.9730	0.9640	-

Table 26

Osmotic Coefficients of Sea Water Solutions (computed)

Temp. t _o	Pressure in. Hg	Salinity, wt %			
		1.70	3.47	5.05	6.59
80.0	13.985	-	0.898	0.931	0.959
85.0	17.070	0.875	0.897	0.928	0.958
90.0	20.703	0.874	0.895	0.926	0.956
95.0	24.961	0.873	0.894	0.923	0.953
100.0	29.921	0.869	0.893	0.921	0.950
105.0	35.672	0.866	0.891	0.919	0.946

Table 27

Osmotic Pressures of Sea Water Solutions, atmospheres

Temp. t _o	Salinity wt %		
deg C	1.70	3.47	5.05
80.0		28.8	43.5
100.0	14.2	29.8	45.1
			6.59
			59.2
			60.1

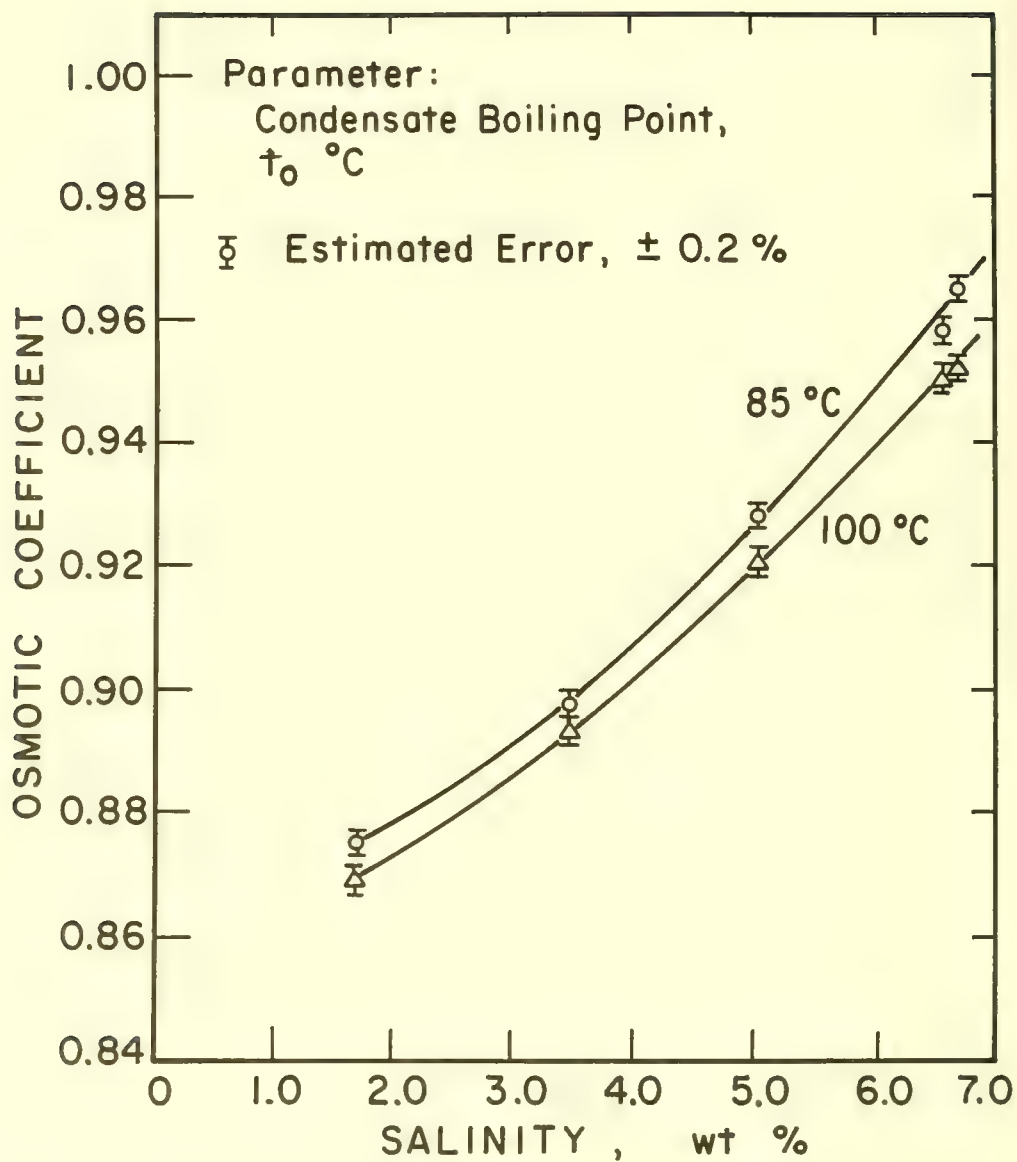


Figure 20
OSMOTIC COEFFICIENT VS. SALINITY

increases, activity of water decreases, the non-ideality increasing with concentration. The derivative of activity with salinity increases and hence we expect BPE to have an increasing slope with increase in concentration. This increase in non-ideality is brought about by the increase in short range interactions. Theoretical predictions of activity coefficients have not been successful, except in the very dilute cases. Empirical extensions of the Debye-Hückel theory are available, which are reasonable, in the concentration range of interest.

The variation of BPE with temperature follows the variation of activity with temperature and pressure (since the pressure also changes with temperature to maintain equilibrium). The variations with pressure are negligible, since the compressibilities of the solution are small. The variation with temperature is governed by the heats of vaporization and solution. This deviates a little from linear as seen in Figure 18.

The osmotic and activity coefficients are strong functions of salinity. In the low concentration regions, where Debye-Hückel theory is valid, the long range ion-ion interactions tend to lower the activity coefficients, according to the Debye-Hückel limiting law. For a mixture like sea water, where there is a large amount of 2-2 and higher valence electrolytes, the concentration range where Debye-Hückel limiting law holds is rather low (less than 10^{-4} molar solutions). The short range forces, such as ion-solvent interactions, start dominating, even at a low concentration. As the concentration increases, the dielectric constant of the medium is decreased. Also there are structural changes in the solution. These short range forces tend to increase the osmotic and activity coefficients.

Thus, a minimum is expected in the osmotic coefficient. This is not very clear in the present work since the concentrations considered are far too high, i.e. the interactions neglected in Debye-Hückel theory dominate in even the lowest concentrations considered here, and all the values observed are in the increasing osmotic coefficient region.

Further data at lower concentrations (less than 0.3% salinity) should show a minimum in the osmotic coefficient -- with the osmotic coefficient of pure water equal to 1.0.

However, the percent error of the BPE determinations, hence osmotic coefficient determination, is larger at lower salinities. Hence, measurements below 0.3% salinities would be much less accurate.

The BPE data obtained in this work have been compared with some of the recently published data on boiling point elevations of sea water solutions. Figure 21 shows a comparison of the various data, typically at 100°C. The relative values are the same at the other temperatures.

Stoughton and Lietzke (13), used osmotic coefficients of synthetic sea salt solutions measured at 25°C to evaluate the constants of their empirical extension of the Debye-Hückel equation. Their values come nearest to the observed values, within 0.5 to 1.0%, deviating more at the higher concentrations. Their empirical expression seems to be a good approximation to the actual values, though not accurate to $\pm 0.001^\circ\text{C}$.

Fabuss and Korosi (14) assumed that the relative molal vapor pressure depressions of the solutes can be added to give the total contribution for the vapor pressure depression of the solution. From this they computed the boiling point elevations. At higher concentrations, their assumption is not valid, as seen from Figure 21. Moreover, they report BPE's to an accuracy of $\pm 0.01^\circ\text{C}$ only.

Grunberg (15) computes BPE's from vapor pressure depression data obtained experimentally on sea water. He used "Ca free" sea water, which was kept in a bath whose temperature was maintained to only $\pm 0.01^\circ\text{C}$. These values are corrected for "Ca" to get values for natural sea water. He also reports BPE data to $\pm 0.01^\circ\text{C}$. The deviations at the higher concentrations are rather large.

Lindsay and Liu (16,17) very recently measured the vapor pressure of simulated sea water in concentration ranges above 1.5 normal sea water. They have used their experimental values to fit a double polynomial in salinity and temperature to the BPE data obtained. A comparison of the actual data obtained by them with the data obtained in present work is given in Table 28. There is a large variation between the data of Lindsay and Liu and this work. One of the reasons might be the replacement of Ca^{++} ions by Mg^{++} ions. Much data has been taken by Lindsay and Liu in comparatively higher temperature and concentration ranges under which conditions CaSO_4 would have precipitated out of

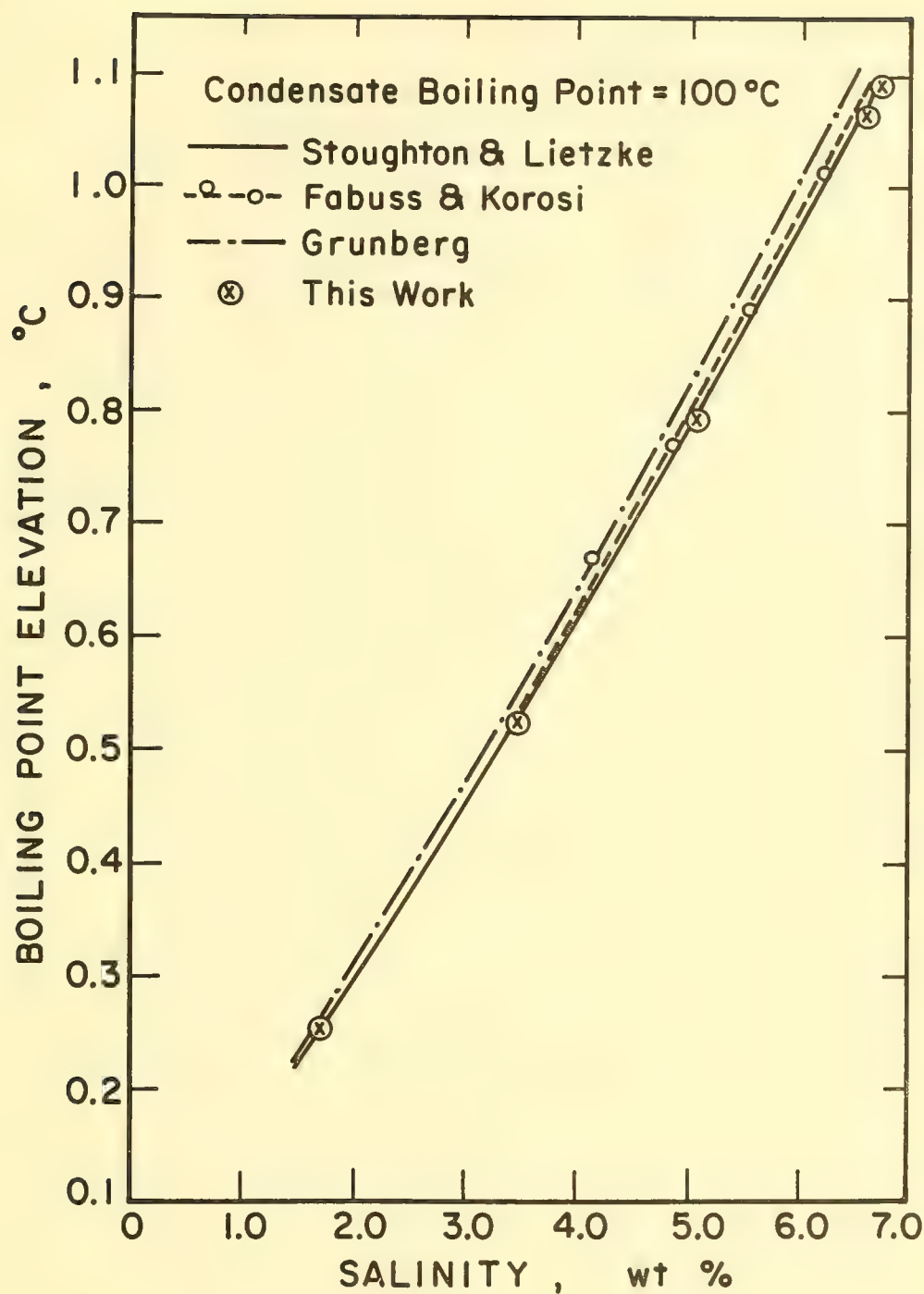


Figure 21

BPE VS. SALINITY, COMPARISONS

Table 28

Comparison with Data of Lindsay and Liu (16,17)

Temp. °C	Salinity	BPE Obs. °C	Lindsay and Liu's f Factor	BPE °C Calculated by Lindsay and Liu Expression
80	33.528	0.447	0.9665	0.407
"	34.67	0.461	0.9994	0.422
"	50.436	0.697	1.4538	0.632
100	33.540	0.505	0.9668	0.469
"	34.73	0.524	1.0011	0.487
"	50.648	0.790	1.4600	0.729
"	67.165	1.088	1.9361	0.994
"	67.369	1.090	1.9420	0.997
110	33.577	0.536	0.9679	0.502

Table 29

Self Consistency of Lindsay and Liu's Data (16,17)

Temp. °C	Lindsay and Liu's f factor	BPE Obs. by Lindsay & Liu °C	BPE °C Calculated by Lindsay and Liu Expression	Deviation °C
	1.4884	0.722	0.745	0.022
100	2.8228	1.541	1.542	0.001
	5.8377	3.576	3.667	0.091

actual sea water. In fact, data for triple concentrated sea water could not be obtained even at 100°C, due to slow precipitation of CaSO_4 during the run. Another apparent reason for variations with Lindsey and Liu's results is that their method of fitting data to a polynomial shows a standard deviation of 0.017°C. Lindsey and Liu fit their data at first to a second degree polynomial in concentration at fixed temperature. However, the maximum number of data points at any temperature is only three. After the coefficients of power series in concentration were determined, the coefficients were fitted to a polynomial in temperature.

VISCOSITY OF SEA SALT SOLUTIONS

Preliminary work has been reported previously (2). The viscometer used was of the glass capillary type and is shown in Figure 22. Figure 23 shows the viscometer above the constant temperature silicone oil bath. Complete details of the system, its operation and results have been recorded (18).

There were two main difficulties in measuring the viscosity of sea salt solutions. First, much of the temperature range to be investigated is above the boiling point of water and hence the system has to be pressurized. Second, natural sea water contains enough calcium and sulfate ions that precipitation may occur at high temperatures and concentrations. If this were allowed to occur the results would be erratic. The problem was avoided by precipitating and filtering the solution.

Measurements of the viscosity of synthetic sea water is contained in work by Fabus et al. (19) and Grunberg (15).

Kinematic Viscosity from Experimental Data

The equation used to calculate the kinematic viscosity from the measured times of flow (t) is

$$V = Ct - \frac{E}{t^2} \quad (21)$$

where C and E are constants nearly independent of flow rate and temperature. The complete derivation is given by Chen (18).

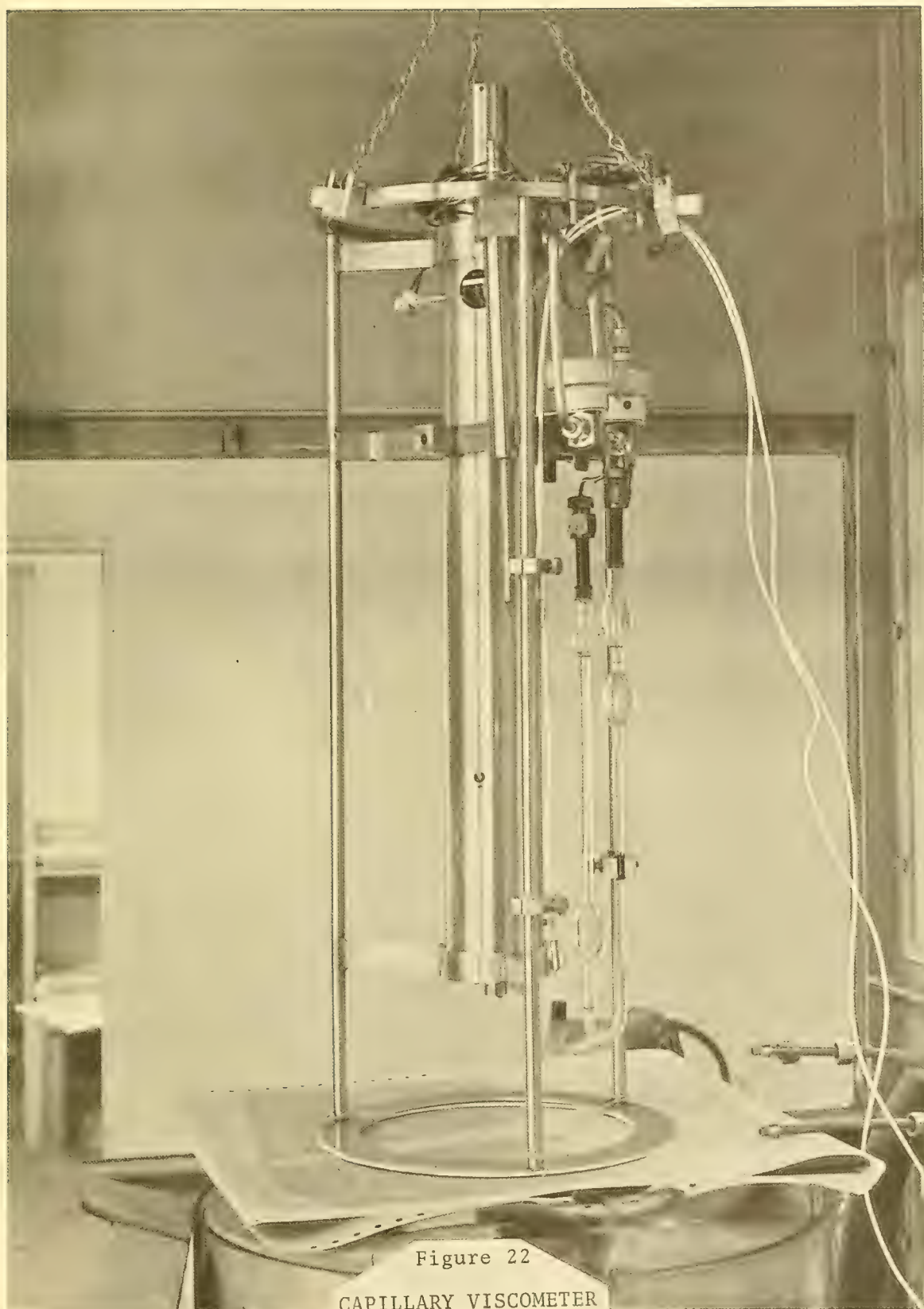




Figure 23

CAPILLARY VISCOMETER ABOVE CONSTANT TEMPERATURE BATH

The calculated values of the kinematic viscosity of distilled water agreed with accepted values to within better than two parts per thousand.

Pressurized System

Figure 24 shows the essentials of the pressurized system. "A" and "B" are Whitey air operated valves, "A" being a normally shut valve which served to isolate the main part of the system inside the oil bath from the remainder outside at ambient temperature. Parts below the dotted line in the figure are inside the oil bath. "A" prevented loss of liquid from the viscometer by condensation in the cooler outside line. "B" was a normally open valve and was used to raise the test liquid into the efflux bulb to obtain a reading. This type of valve was chosen because it was capable of operating immersed in silicone oil at temperatures up to 150°C. Compressed air from a cylinder and two solenoid valves were used to operate "A" and "B".

On the right in the diagram the system ended in a closed chamber consisting of a 1" diameter hole drilled in a 2" cube of stainless steel. It had provision for a pressure transducer and was closed at the far end by a 2"-diameter plate and o-ring. All connections were done with 1/4" stainless steel tube and Swagelok fittings except for the tubes immediately connected to the viscometer. These were of 1/8" tube to provide some flexibility since the connections to the viscometer had to be bent until they fitted without putting any strain on the glass.

While the bath temperature was being altered or while waiting for the bath temperature to become steady, "A" was closed, "B" was open and the test liquid was in the receiving bulb. To take a reading, "A" was opened, "B" closed, and compressed air from a cylinder used to push the liquid into the efflux bulb. Once the liquid reached the fill mark, the pressure in both arms was equalized by opening "B", "A" was closed and the liquid allowed to run back into the receiving bulb. It was estimated that there was ample time for the pressure in both arms to equalize before the meniscus reached the first timing mark, "C".

The closed chamber on the right provided some buffer volume to prevent the pressure in the efflux arm from becoming too great as the liquid was raised. For readings up to 80°C, where evaporation was less severe, the pressure in the system was released after each reading by opening "A"

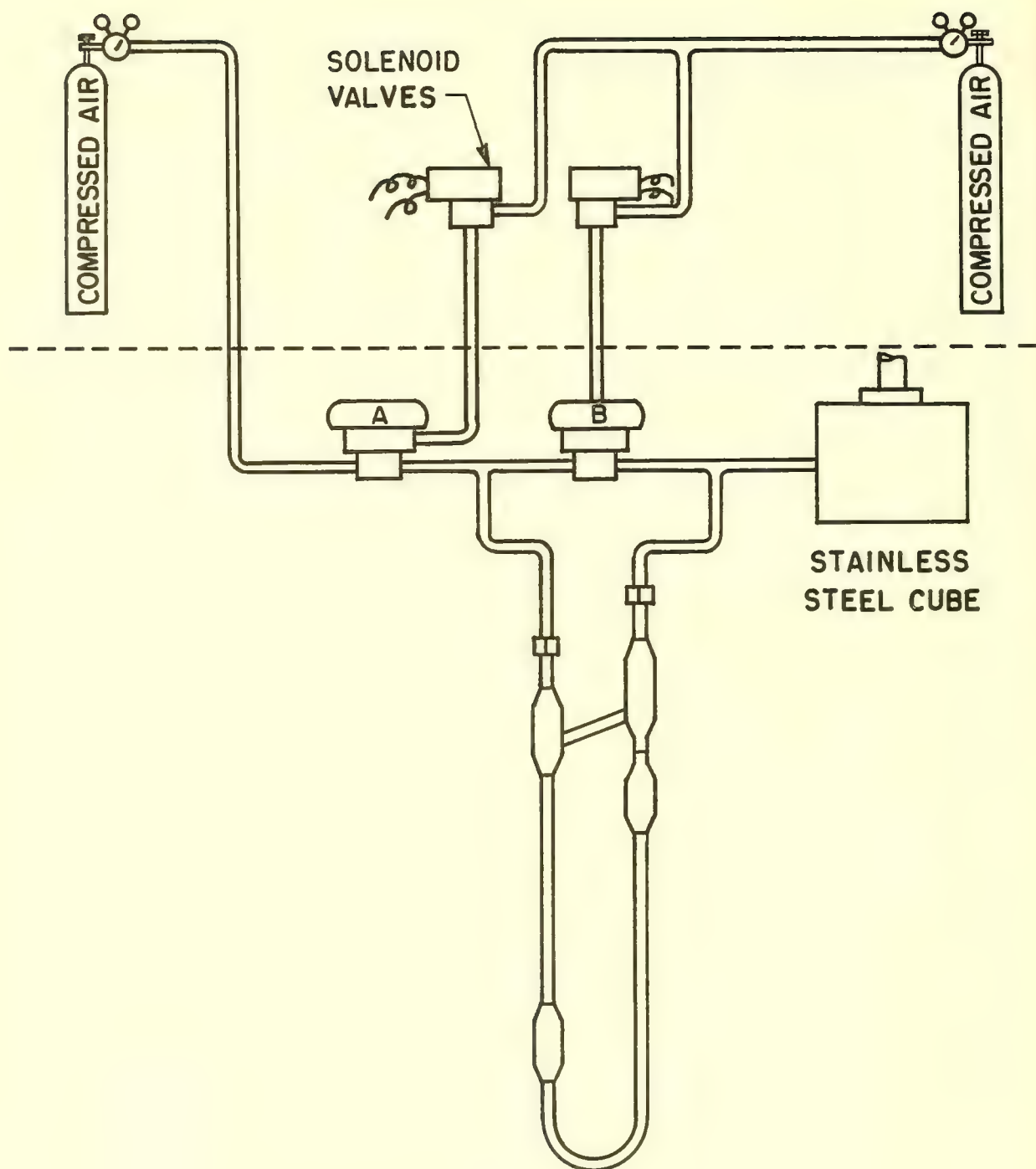


Figure 24

PRESSURIZED SYSTEM FOR VISCOSITY MEASUREMENT

and another valve close to the regulator on the cylinder of compressed air. After 80°C, the pressure was not released and continued to rise with each successive reading until it was usually between 70 and 80 psig for the final reading at 150°C.

Work by Korosi and Fabuss (20) and Bridgman (21) indicate that pressures of up to 100 psig would have a negligible effect on the viscosity of water. This was checked by taking readings at the lower temperatures with varying pressures. After correction for the vapor column, there was no significant variation among the various viscosity values.

Initially, the closed chamber was not only intended to provide buffer volume. It had been intended to accomodate a silver/palladium membrane in the form of a narrow tube wound in a spiral and with the end inside the chamber sealed. The other end was left open and was led out through the back plate to a vacuum line. With this, hydrogen could be substituted for air in the system and the liquid raised by diffusing hydrogen through the membrane. In this case, no water vapor would be lost. However, the membrane proved very easily poisoned by impurities. When it was first received from the suppliers, it could not pass any hydrogen at all and had to be returned for re-activation. The second time it was received it did work but by then it had been decided to continue with the alternative method.

Constant Temperature Bath

The oil bath consisted of approximately 12 gallons of Dow Corning 510 Silicone Oil contained in a glass cylinder surrounded by a larger glass cylinder through which hot air could be circulated. The oil was circulated downward through a central tube contained in the oil bath.

The bath temperature was monitored by two Hewlett Packard quartz thermometer probes and controlled by the resistance thermometer of a Hallikainen Thermotrol. The maximum temperature variation found was 0.08°C and the maximum temperature fluctuation was .02°C. The probes were calibrated at the ice point and were accurate to .02°C absolute and sensitive to better than 0.001°C. Thus the maximum possible temperature uncertainty is 0.1°C.

Filter

The precipitation of calcium sulfate as the temperature increased was the main difficulty in working with natural sea water. If the precipitation was allowed to occur in the capillary, it might become plugged completely or else the readings would have been very erratic. From this point of view therefore, it was impossible to measure the viscosity of natural sea water by this method. The next best thing seemed to be to remove some of the calcium sulfate beforehand by heating the solutions to 150°C and filtering them under pressure. As 150°C was the highest experimental temperature, there was no subsequent precipitation during test runs.

Basically, the filter was a pressure vessel divided into two chambers by a fiberglass filter paper which was supported by wire screens (Figure 25). All metal parts were of 316 stainless steel. Each chamber consisted of a 2" long industrial glass pipe spacer, 2" i.d. with 3/8" wall. These were closed at the outer ends by steel end-pieces, with washers of ethylene-propylene rubber preventing direct contact between the ends of the pipe spacers and the metal end pieces. The seals between the pipe spacers and the end pieces were made by o-rings around the pipe compressed on to the end pieces by circular clamps.

The center piece contained the filter paper held between two wire gauze screens and was shared by both chambers. The method of sealing was the same. The entire assembly was held together by three rods which ran the length of the filter and were bolted across the end pieces. The only difference between chambers "A" and "B" was that there was a capillary tube welded through the center of the endpiece in "B" and this was connected to a small throttle valve on the outside.

To operate, the filter was assembled with chamber "A" almost full of sea water. Then it was held in an oven at 150°C for several hours. To filter, it was inverted so that "A" was then uppermost and the pressure released slightly in "B". A slow release of pressure was enough to drive the liquid through the filter.

Results

Distilled water runs and calibration constants: The calibration constants for the two viscometers used are given below. The viscometer with the swagelok fittings was used

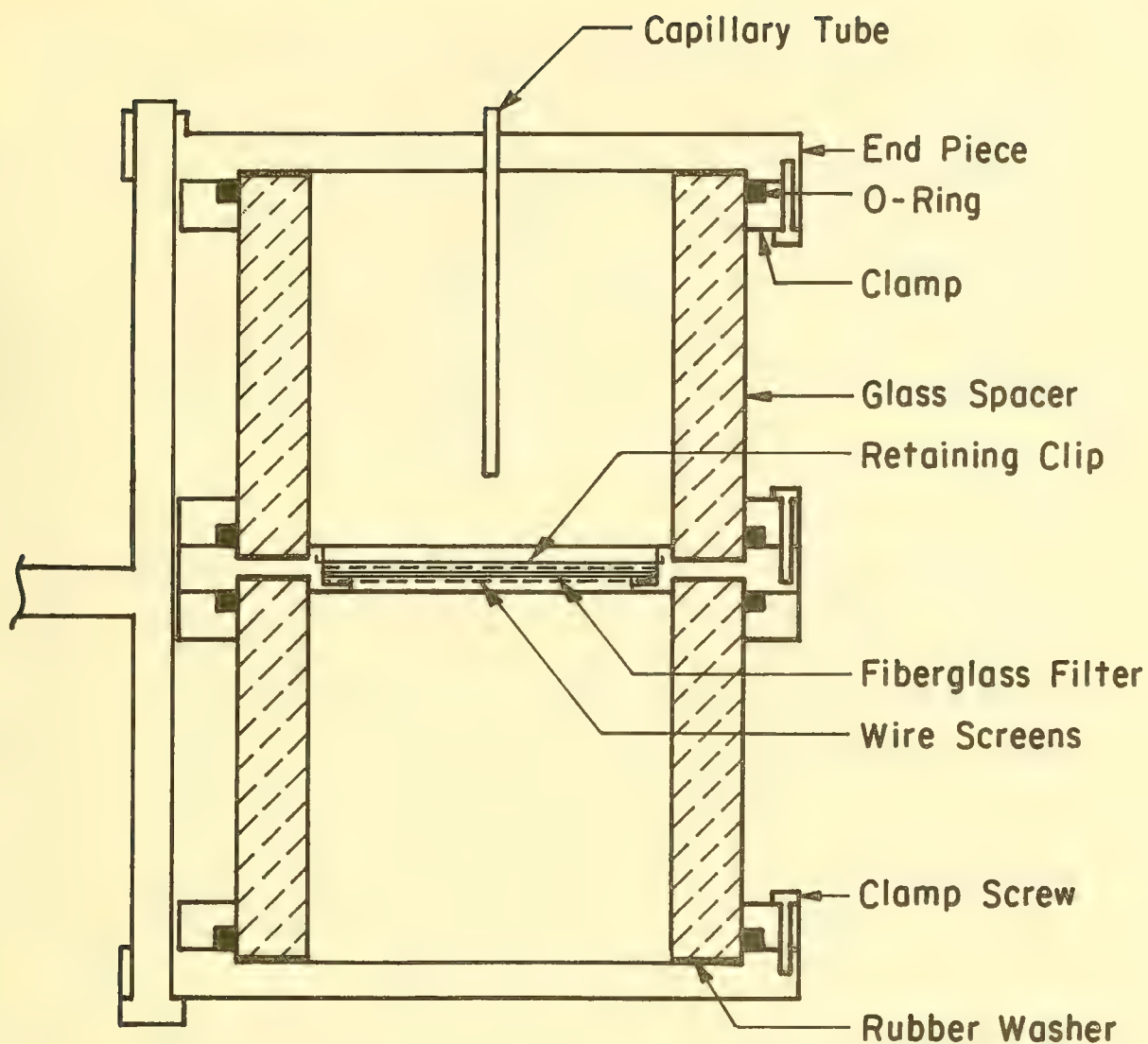


Figure 25
FILTER FOR VISCOSITY MEASUREMENT

for the bulk of the readings. Only the values for sea water of salinity 3.49% were taken with the viscometer with the o-ring fittings. (See equation 27).

<u>Viscometer fitting</u>	<u>C</u>	<u>E</u>
Swagelok	0.0010901	324.0
O-ring	0.0008135	519.3

As a check on the validity of these constants, values for the kinematic viscosity of distilled water were calculated using them and smoothed against the temperature using the equation

$$\log_{10} \nu = A + \frac{B}{T - C} \quad (22)$$

from Kestin and Whitlaw (22). The smoothed values are given in Table 30 and compared with the literature values. Most of the values agree to within one part in a thousand. A disappointment here were the values of viscosity at temperatures below 20°C. When these were included they caused large discrepancies (about 3 parts per 1000) in the smoothed values at 20 and 40°C and the value at 0°C was off by about 1%. However, as taking data at these temperatures required an appreciable effort, it was decided to treat them separately rather than to ignore them. This was done by using the data between 0 and 20°C only to give values at 0 and 10°C. This data did not fit the main correlation from 20 to 150°C, but this treatment seemed to be the best way of dealing with them.

The experimental solutions: Eight different sea water samples were used with salinity varying from 1 to 11%. The method of preparing a sample was first to acidify it to a pH of 4.5 with concentrated sulfuric acid. This removed the bicarbonate ion and prevented the carbonate from precipitating on heating. The next step was to concentrate or dilute to the desired salinity. The solution was then filtered at 150°C to remove some of the calcium sulfate and the concentrations of the Cl^- and Br^- , Ca^{++} and SO_4^{--} ions were determined by gravimetric analysis. The remaining sea water ions were assumed to remain in the same proportion to Cl^- and Br^- as in the typical sea water analysis in Table 7. This was taken from Sverdrup et al. (8). From this information the concentrations of the sea water solutions were expressed in two ways:

Table 30

Comparison of experimental and accepted values
for kinematic viscosity of distilled water

Temperature °C	Expt. Viscosity Cstks	Lit. Viscosity Cstks (24)
0.0	1.789	1.787
10.0	1.306	1.306
20.0	1.0037	1.0038
30.0	1.8016	0.8010
40.0	0.6585	0.6578
50.0	0.5535	0.5532
60.0	0.4744	0.4745
70.0	0.4132	0.4136
80.0	0.3649	0.3648
90.0	0.3261	0.3255
100.0	0.2944	0.2942
110.0	0.2681	0.2679
120.0	0.2461	0.2456
130.0	0.2275	0.2273
140.0	0.2115	0.2117
150.0	0.1978	0.1979

Experimental data fit to $\log_{10} \nu = A + \frac{B}{(T-C)}$ with a

standard deviation of 5×10^{-4} .

Values of A, B, and C with T in °K and ν in centistokes are:

A -1.464

B 205.4

C 153.0

Ionic strength, I:

$$I = \sum_i 1/2 m_i v_i^2 \quad (23)$$

m_i is the moles of ion i per 1000 gm of solution
 v_i is the valency of ion i

Ionic strengths of test solutions ranged from 0.2 to 2.2 with typical sea water at 0.7.

Salinity - Salinity is here defined as the total weight of dissolved salts in solution expressed as a percentage of the total solution weight. Salinities ranged from 1.0 to 11.0% with typical sea water at 3.3%.

In Table 31, the Cl^- and Br^- , Ca^{++} and SO_4^{--} concentrations as well as the salinities and ionic strengths are given for the eight test solutions. Also given are the ratios of Ca^{++} and SO_4^{--} to Cl^- and Br^- . Horne (23) gives these values for the West Pacific Ocean as 0.0206 to 0.0213 for Ca^{++} and 0.140 for SO_4^{--} . The experimental ratios agree with these values to within 5% at the lower salinities, but become much less at the more concentrated solutions due to the removal of calcium sulfate.

Because the salinities were calculated by assuming constant proportions among the various ions, they cannot be considered more accurate than 5%. However, the reproducibility of the results, which depend mainly on the gravimetric analysis of the Cl^- and Br^- is much better than this.

Viscosity: For each of the experimental solutions two separate runs were done from 0 to 150°C. For each run the viscometer was cleaned with aqueous sodium triphosphate followed by chromic acid. It was then filled with sea water and readings taken at the following temperatures (°C) approximately: 0.2, 2.0, 4.0, 10.0, 20, 40, 60, 80, 100, 120, 140, 150.

To produce Table 32 the viscosity values were first corrected for evaporation and then fit by least squares against the salinity using

$$\nu = \nu_{dw} + Ax + Bx^2 + Cx^4 \quad (24)$$

ν is the kinematic viscosity of the solution in centistokes

Table 31

Experimental Solutions

#	Gm/kg solution			Salinity	I
	<u>Cl⁻ & Br⁻</u>	<u>SO₄⁻⁻</u>	<u>Ca⁺⁺</u>		
1	5.57	0.78	0.12	1.00	0.200
2	16.29	2.35	0.35	2.95	0.589
3	19.27	2.77	0.40	3.49	0.697
4	26.29	3.80	0.54	4.76	0.950
5	33.41	4.65	0.54	6.00	1.189
6	41.31	5.48	0.77	7.41	1.470
7	51.26	6.26	0.75	9.11	1.802
8	63.24	6.92	0.60	11.13	2.190

#	<u>SO₄⁻⁻</u>	<u>Ca⁺⁺</u>
	<u>Cl⁻ & Br⁻</u>	<u>Cl⁻ & Br⁻</u>
1	0.140	0.0215
2	0.144	0.0215
3	0.144	0.0208
4	0.145	0.0205
5	0.139	0.0161
6	0.133	0.0186
7	0.122	0.0146
8	0.109	0.0095

Table 32

Kinematic Viscosity of Sea Water Solutions, centistokes

Temp. °C	% Salinity											σ
	1	2	3	4	5	6	7	8	9	10	11	
0	1.803	1.809	1.817	1.821	1.829	1.844	1.862	1.885	1.911	1.941	1.975	2.014 2×10^{-3}
10	1.324	1.334	1.345	1.349	1.357	1.372	1.389	1.409	1.431	1.456	1.483	1.513 2×10^{-3}
20	1.0207	1.0311	1.0421	1.0459	1.0542	1.0677	1.0828	1.0995	1.1179	1.1380	1.1599	1.1836 1×10^{-3}
30	0.8173	0.8268	0.8364	0.8398	0.8469	0.8586	0.8714	0.8856	0.9012	0.9182	0.9366	0.9564
40	0.6727	0.6812	0.6898	0.6927	0.6990	0.7092	0.7203	0.7326	0.7459	0.7604	0.7761	0.7929 7×10^{-4}
50	0.5662	0.5739	0.5817	0.5843	0.5899	0.5989	0.6087	0.6194	0.6310	0.6435	0.6570	0.6715
60	0.4857	0.4928	0.4998	0.5022	0.5072	0.5153	0.5240	0.5334	0.5436	0.5546	0.5664	0.5789 7×10^{-4}
70	0.4233	0.4298	0.4363	0.4384	0.4430	0.4503	0.4581	0.4666	0.4756	0.4853	0.4957	0.5067
80	0.3740	0.3800	0.3860	0.3880	0.3922	0.3988	0.4059	0.4135	0.4216	0.4303	0.4395	0.4493 5×10^{-4}
90	0.3343	0.3399	0.3454	0.3473	0.3512	0.3573	0.3638	0.3707	0.3780	0.3858	0.3941	0.4028
100	0.3019	0.3071	0.3122	0.3140	0.3176	0.3232	0.3292	0.3355	0.3422	0.3493	0.3568	0.3647 4×10^{-4}
110	0.2750	0.2798	0.2847	0.2863	0.2897	0.2950	0.3005	0.3063	0.3125	0.3190	0.3258	0.3329
120	0.2524	0.2570	0.2616	0.2631	0.2663	0.2712	0.2764	0.2818	0.2875	0.2934	0.2997	0.3062 3×10^{-4}
130	0.2333	0.2376	0.2420	0.2434	0.2464	0.2511	0.2559	0.2609	0.2662	0.2717	0.2775	0.2835
140	0.2169	0.2210	0.2251	0.2265	0.2294	0.2338	0.2383	0.2430	0.2480	0.2531	0.2584	0.2639 9×10^{-4}
150	0.2027	0.2067	0.2106	0.2119	0.2146	0.2188	0.2231	0.2276	0.2322	0.2370	0.2419	0.2470 1×10^{-3}
σ	1×10^{-4}	2×10^{-4}	4×10^{-4}	4×10^{-4}	6×10^{-4}	7×10^{-4}	8×10^{-4}	8×10^{-4}	8×10^{-4}	7×10^{-4}	6×10^{-4}	4×10^{-4}

ν_{dw} is the kinematic viscosity of distilled water at the same temperature.

x is the square root of the salinity

A, B, C are empirical constants (Table 33)

The values of σ in the extreme right hand column of Table 32 give a measure of agreement between Equation 24 and the experimental data where

$$\sigma = \left[\frac{\sum_{i=1}^N (\nu_i - (\nu_{dw} + Ax_i + Bx_i^2 + Cx_i^4))^2}{(N - 3)} \right]^{1/2} \quad (25)$$

in which ν_i , x_i^2 are the viscosity and salinity for the i 'th data point respectively and N is the number of points.

In doing this, the values of viscosity for sample number 5 were not used, as they seemed to be too far from the curve along which the rest of the data lay. Values of viscosity at even values of salinity were calculated (Eq. 1 of (18)). These values were fit by least squares against the temperature using

$$\log_{10} \nu = A' + \frac{B'}{(T - C')} \quad (26)$$

where T is the absolute temperature and A' , B' , C' are empirical constants.

The viscosities at 10 and 0°C are obtained as described in the section on distilled water results. The values of σ given in the bottom row of Table 32 were similarly defined. The viscosity values at the same temperature and salinity were also calculated by fitting the data against the temperature first and then the salinity but the results were the same to within 0.0001. For comparison, Tables 34-41 give the original viscosity data.

Error Analysis:

1. Error in temperature measurement:

Worst case (at 150°C): $\pm 0.1^\circ\text{C}$

Typical case (at 80°C): $\pm 0.05^\circ\text{C}$

2. Error in salinity measurement: Experimental error of Cl and Br determination by gravimetric analysis is ± 0.01 , but systematic error of assuming constant proportions among

Table 33

Values of Empirical Constants of Equation 24

t°C	A	B	C
20	1.497×10^{-2}	1.018×10^{-3}	9.793×10^{-4}
40	1.245 "	1.800 "	6.163 "
60	8.067×10^{-3}	2.594 "	4.062 "
80	6.593 "	2.314 "	3.079 "
100	4.908 "	2.436 "	2.243 "
120	5.193 "	1.656 "	2.056 "
140	2.252 "	2.780 "	1.200 "
150	1.194 "	3.449 "	5.937 "

Table 34
Original data for water, salinity 1.00

Temp. Deg.C	Viscosity Cstks.	Temp. Deg.C	Viscosity Cstks.
19.993	1.0216	119.993	0.2527
19.996	1.0215	140.064	0.2174
20.006	1.0196	150.060	0.2034
20.006	1.0191	60.069	0.4849
40.022	0.6723	60.069	0.4849
40.022	0.6723	80.277	0.3723
40.034	0.6723	80.277	0.3724
40.034	0.6718	99.992	0.3016
60.008	0.4850	99.992	0.3016
60.008	0.4854	110.033	0.2746
79.919	0.3743	110.033	0.2747
79.919	0.3741	120.015	0.2525
99.958	0.3019	140.067	0.2170
99.958	0.3017		
110.032	0.2748		
110.032	0.2750		
0.195	1.7922	0.187	1.7926
2.149	1.6798	2.097	1.6827
6.293	1.4747	4.078	1.5783
9.837	1.3303	9.888	1.3279

Already corrected for evaporation.

Table 35
Data for sea water, salinity 2.95

Temp. Deg.C	Viscosity Cstks.	Temp. Deg.C	Viscosity Cstks.
0.021	1.8079	4.213	1.5907
0.021	1.8080	0.258	1.8027
2.232	1.6905	2.169	1.6934
2.232	1.6901	6.073	1.5031
4.193	1.5907		
19.994	1.0420	80.271	0.3847
19.994	1.0400	99.951	0.3121
20.062	1.0390	99.951	0.3125
20.062	1.0398	109.986	0.2846
20.062	1.0399	109.986	0.2846
20.056	1.0398	119.981	0.2617
30.089	0.8353	140.043	0.2251
39.978	0.6902	150.034	0.2102
39.926	0.6903	150.034	0.2106
39.926	0.6908	59.998	0.4998
40.016	0.6899	59.998	0.4996
40.016	0.6896	80.274	0.3847
59.981	0.4999	80.274	0.3843
80.280	0.3843	99.991	0.3117
100.250	0.3108	99.991	0.3114
119.972	0.2611	110.021	0.2839
140.029	0.2242	110.021	0.2842
150.024	0.2096	119.987	0.2610
59.943	0.4995	140.047	0.2246
59.939	0.4995	150.040	0.2106

Corrected for evaporation.

Table 36
Data for sea water, salinity 3.49

Temp. Deg.C.	Viscosity Cstks.	Temp. Deg.C	Viscosity Cstks.
2.263	1.6967	10.123	1.3482
20.003	1.0493	100.033	0.3149
20.003	1.0473	100.033	0.3148
20.003	1.0485	100.015	0.3146
40.045	0.6951	100.015	0.3147
40.045	0.6951	120.144	0.2633
60.056	0.5042	120.144	0.2634
60.056	0.5044	140.098	0.2264
80.314	0.3880	140.098	0.2267
80.314	0.3885	150.087	0.2122
		150.087	0.2120

Corrected for evaporation.

Table 37
Data for sea water, salinity 4.76

Temp. Deg.C	Viscosity Cstks.	Temp. Deg.C	Viscosity Cstks.
2.151	1.7241	2.034	1.7235
6.038	1.5280	4.066	1.6175
9.846	1.3728	9.886	1.3702
0.219	1.8247		
20.000	1.0626	120.025	0.2692
20.000	1.0632	120.025	0.2692
19.993	1.0627	140.104	0.2318
19.993	1.0626	150.100	0.2204
40.086	0.7062	60.090	0.5127
40.086	0.7064	60.090	0.5127
40.046	0.7063	80.326	0.3955
40.046	0.7062	80.326	0.3955
60.104	0.5126	80.326	0.3956
60.104	0.5128	100.031	0.3212
80.343	0.3956	100.031	0.3214
80.343	0.3955	120.036	0.2693
100.048	0.3213	120.036	0.2693
100.048	0.3214		

Table 38
Data for sea water, salinity 6.00

Temp. Deg.C	Viscosity Cstks.	Temp. Deg.C	Viscosity Cstks.
0.168	1.8677	7.469	1.5028
0.170	1.8679	0.129	1.8724
1.987	1.7644	1.962	1.7697
2.001	1.7641	6.582	1.5429
4.031	1.6595	9.364	1.4279
19.908	1.0939	99.961	0.3322
19.903	1.0950	109.998	0.3031
19.939	1.0954	109.998	0.3030
19.952	1.0952	119.994	0.2786
40.010	0.7286	130.033	0.2578
40.010	0.7294	60.016	0.5303
40.015	0.7292	60.016	0.5301
40.015	0.7292	79.913	0.4105
59.938	0.5309	79.913	0.4107
59.938	0.5309	99.959	0.3324
80.266	0.4089	99.959	0.3326
80.266	0.4089	119.981	0.2785
99.961	0.3323	140.058	0.2401
		150.055	0.2247

Corrected for evaporation.

Table 39
Data for sea water, salinity 7.41

Temp. Deg.C	Viscosity Cstks.	Temp. Deg.C	Viscosity Cstks.
0.214	1.8828	0.216	1.8843
2.057	1.7789	2.056	1.7809
6.062	1.5811	4.094	1.6755
9.876	1.4225	9.885	1.4249
20.021	1.1073	120.048	0.2833
20.021	1.1074	120.048	0.2834
20.023	1.1054	140.104	0.2450
20.023	1.1052	150.092	0.2303
40.089	0.7390	60.106	0.5374
40.089	0.7387	60.106	0.5376
40.083	0.7380	80.321	0.4155
40.083	0.7378	80.321	0.4156
60.094	0.5381	100.027	0.3383
60.094	0.5381	100.027	0.3384
80.328	0.4157	120.043	0.2836
80.328	0.4158	120.043	0.2837
100.028	0.3378	140.990	0.2457
100.028	0.3379	150.102	0.2309

Corrected for evaporation.

Table 40
Data for sea water, salinity 9.11

Temp. Deg.C	Viscosity Cstks.	Temp. Deg.C	Viscosity Cstks.
2.828	1.7845	6.043	1.6241
2.064	1.8222	6.042	1.6225
4.100	1.7150	9.901	1.4593
4.079	1.7199	9.897	1.4618
20.038	1.1378	80.348	0.4288
20.038	1.1384	80.357	0.4294
20.033	1.1377	80.357	0.4295
20.033	1.1372	100.064	0.3496
20.033	1.1375	100.064	0.3494
40.064	0.7613	100.071	0.3490
40.064	0.7610	100.071	0.3490
40.072	0.7615	120.042	0.2928
40.072	0.7612	120.042	0.2926
60.110	0.5554	120.029	0.2933
60.110	0.5555	120.029	0.2934
60.124	0.5539	140.111	0.2533
60.124	0.5539	140.130	0.2523
60.124	0.5539	150.094	0.2370
80.348	0.4287	150.094	0.2368
80.348	0.4286	150.071	0.2367

Corrected for evaporation.

Table 41
Data for sea water, salinity 11.13

Temp. Deg.C	Viscosity Cstks.	Temp. Deg.C	Viscosity Cstks.
0.602	1.9824	2.029	1.8977
2.051	1.8975	6.068	1.6885
4.036	1.7921	12.527	1.4204
0.185	2.0069		
20.021	1.1867	109.991	0.3341
20.021	1.1868	119.974	0.3072
20.105	1.1838	140.036	0.2651
20.105	1.1835	150.032	0.2482
39.995	0.7970	59.997	0.5807
39.995	0.7970	59.997	0.5809
40.016	0.7949	80.300	0.4489
40.016	0.7949	100.008	0.3652
59.967	0.5817	100.008	0.3654
59.967	0.5815	110.026	0.3339
80.263	0.4502	110.026	0.3340
80.263	0.4502	120.000	0.3070
99.973	0.3663	140.058	0.2650
99.973	0.3658	150.053	0.2479
109.991	0.3342		

Corrected for evaporation.

sea salts is 5%.

3. Timing error: The stopwatch was accurate to 0.1 seconds. For repeated readings at the same temperature in the same run, timing error was 0.1%.

4. Error in calibration constant, C, was 0.1% from different distilled water runs.

5. Error in calibration constant, E, was 3%.

6. Error in thermal expansion correction: $2 \times 10^{-7}\%$ at 80°C and $4 \times 10^{-7}\%$ at 150°C .

7. Error in vapor column correction: Most of the error is in pressure gauge which was accurate to .5%. Resulting error in correction was 3×10^{-7} at 80 and $2 \times 10^{-6}\%$ at 150°C .

The equation used to calculate the viscosity was

$$\nu = Ct \cdot \text{cor } 1 \cdot \text{cor } 2 - \frac{E}{t^2} \quad (27)$$

where cor 1 was the thermal expansion correction, cor 2 was the vapor column correction, t was the time in seconds, and C and E were the calibration constants.

The effect of uncertainties in these quantities led to the following uncertainties in the viscosity:

At 80°C 0.0006
At 150°C 0.0003

The effect of the uncertainty in temperature was obtained by differentiating Equation 26 with respect to temperature

$$\frac{d\nu}{dT} = \nu \cdot \frac{2.3B'}{(T-C')^2} \quad (28)$$

For typical sea water, salinity 3.3, the following errors were found:

At 80°C 0.0003
At 150°C 0.0001

These errors did not change appreciably with salinity.

The effect of the experimental uncertainty in salinity was found by differentiating Equation 24 with respect to x

$$\frac{dv}{dx} = A + 2Bx + 4Dx^3 \quad (29)$$

At 80° C the following errors were found:

Salinity 3.3	0.00009
Salinity 11.0	0.0001

These errors did not change appreciably with temperature.

The estimated error in the viscosity was ± 0.001 . This was somewhat larger than most of the standard deviations obtained for the fitted data.

Conclusions

The apparatus was disappointing, as the precision of the results was ± 0.001 centistokes. A precision of ± 0.0001 centistokes had been hoped for in order to work with electrolyte solutions made up in the lab. Improvements that can be made on the existing apparatus are:

1. Use of the silver/palladium probe to obtain a constant high pressure for all the readings. Using the probe necessitates the use of hydrogen in the system which would reduce the vapor column correction.
2. Improvement of the temperature control in the bath. One possibility is to put fiberglass insulation around the oil bath and use the hot air outside that.
3. Use of a photocell device to time the viscometers.

Comparison with the work of Korosi and Fabuss (20) and Grunberg (15) showed agreement in the viscosity at the same ionic strength to within 2%. In preparing their test solutions, Grunberg left out the Ca^{++} completely whereas Korosi and Fabuss replaced it with equivalent Mg^{++} . In increasing viscosity values the order was (1) Grunberg (as would be expected), (2) Korosi and Fabuss, and (3) the present work. The agreement between the last two was better than with the first, but one would have expected a reverse order. A possible explanation is the organic material in natural sea water.

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